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SEMI-ANNUAL PROGRESS REPORT

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STUDIES OF THE FUNDAMENTAL CHEMISTRY,
PROPERTIES, AND BEHAVIOR OF FUEL CELLS

NSG-325

Submitted to:

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Submitted by:

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I. DETERMINATION OF POINTS OF ZERO CHARGE

1. Introduction

During the present report period, the radiotracer method for investigation of adsorption was used for determination of points of zero charge (PZC) as devised by Green and Dahms.¹ The principle of the method has been described in a previous report.²

The method was modified to some extent in order to attain an overall higher accuracy needed in the determination of organic adsorption curves for the PZC method where precise location of adsorption versus potential curves is required.

2. Experimental Modifications

The counter-electrode in a sidearm was replaced by a cylindrical platinum wire gauze which surrounds the tape. This resulted in a much more uniform current density distribution and thus a uniform potential difference across the metal-solution interface.

The D.C. amplifier circuit was discarded as it was not able to potentiostat the tape electrode with sufficient accuracy. It was replaced by a Wenking potentiostat and a Keithley electrometer. This arrangement gives a closer potential control and accurate measurements of potential difference between the reference electrode and the tape.

Except for these improvements the method is essentially the same as previously used.

3. Experimental and Results

The metals studied were nickel and platinum.

Nickel:

The pretreatment given to nickel tapes was as follows: The tape as received from American Silver Company was washed with acetone, then vapor degreased with trichloroethylene for 30 minutes. The tape was then chemically etched in 1:1 hydrochloric acid for five minutes at 35°C and then washed with distilled water before mounting in the apparatus.

The cleaning compartment was filled with 0.01 N hydrochloric acid and the adsorption compartment of the cell was filled with solutions of appropriate concentrations of sodium perchlorate at pH \sim 13 and labeled naphthalene. The tape was kept in the cleaning compartment for one-half hour to remove oxide formed during handling. While the tape was moving into the adsorption compartment, it was washed with deaerated distilled water to remove any chloride ion adhering to the tape. It was necessary to have the distilled water free from oxygen since it was determined that further unwanted oxidation can occur in the washing step if this precaution is not observed. With oxide, the adsorption maximum shifts to a more cathodic potential (cf. Figs. 1 and 2).

The adsorption curves on nickel were determined for electrolyte concentrations of 0.1 and 0.01 N NaClO_4 . The PZC is shown to be -340 mv with respect to N.H.E. Adsorption curves and the PZC intersection are shown in Fig. 2. The above result is in good agreement with PZC obtained

by Krasikov and Sysoeva³ by capacitance measurements.

Platinum:

A doubly clad platinum on nickel tape was used. The tape was washed with acetone and then degreased with trichloroethylene for 30 minutes. It was treated further with 1:4 nitric acid, sulphuric acid mixture, washed with water and then threaded through the cell.

The solution in the cleaning compartment was 0.01 N HClO_4 and the adsorption cell contained 1.6×10^{-5} M naphthalene together with the appropriate concentration of sodium perchlorate at a pH 12. A long cathodic pulse (5 min) was given at very low current density (0.1 mA cm^{-2}). The tape was washed with deaerated distilled water before entering into the adsorption compartment.

The adsorption curves were determined for electrolyte concentrations of 1 N, 0.3 N and 0.1 N NaClO_4 . The PZC obtained from intersection of the adsorption vs potential curves (cf. Fig. 3) for these three electrolyte concentrations is -40 mv (N.H.E.). This agrees reasonably well with Krasikov and Kheifets⁴ who measured PZC on platinum by a capacity method.

Experimentation is presently concentrated on adsorption-potential determinations for gold. To date, good agreement has been obtained in comparison with the work of Dahms and Green¹ for similar NaClO_4 electrolytes. Work is in progress to determine further adsorption-potential curves for other concentrations for precise location of the PZC.

II. ELECTROCATALYSIS

1. General

The field of electrocatalysis of importance to fuel cell research has been reviewed and material prepared for publications. In the appendix (Appendix 1) the factors affecting the rates of chemical and electrochemical reactions are analyzed. The difference between chemical and electrochemical catalysis arising from the existence of an applied field and from the presence of solvent is discussed from the theoretical and experimental point of view. A discussion of the ways to enhance electrocatalysis is presented.

The mechanisms of several electrode reactions (oxidation of hydrogen, hydrocarbons, oxalic acid, oxygen reduction) pertinent to fuel cell reactions are discussed, as a prerequisite to considerations of catalysis.

An attempt is made to formulate some aspects of the mechanism of catalysis for the hydrogen evolution and hydrocarbon oxidation reactions.

The needed trends in research are discussed. Details are given in the attached paper (Appendix 1).

2. Electrochemical Kinetics of Parallel Reactions

The electrochemical oxidation of complex substances, e.g., higher hydrocarbons may involve parallel reactions yielding partial or other oxidation products in addition to complete oxidation products. If such parallel reactions take place, the efficiency of a fuel cell,

using these reactants as fuels will be lowered. Coulombic yields in parallel reactions may or may not vary with potential. In the case where coulombic yields vary with potential over certain potential ranges, the complete oxidation product may result. A theoretical analysis of the different possible cases in parallel reactions was carried out and the variation of coulombic yields with potentials in each case was considered. Details are given in attached paper (Appendix 2).

3. Future Work

The potential sweep method has been widely used experimentally in recent times to study mechanisms of interest in fuel cell research. However, though a vast amount of experimental data is available, they have not been interpreted to yield information on the mechanism of the reactions studied. The method is being theoretically investigated from the point of view of ascertaining its usefulness in obtaining the mechanisms of reactions.

III. CATALYTIC ACTIVITY FOR SIMPLE ELECTRODE REACTIONS

1. Introduction

Although it has been known for some time that the electrode substrate can affect the electrochemical rate of a reaction, little effort has been made until recently to analyze what are the major factors, or what properties of the substrate affect the rate of a reaction. Conway and Bockris,⁵ for instance, have observed a direct relationship between the work function and $\log i_0$ for the hydrogen evolution reaction on a number of metals. This study illustrates the importance of a systematic study in determining major factors which affect electrocatalysis.

It is convenient to divide the possible factors affecting the rate of a reaction into two major categories: geometric and electronic factors. Geometric factors include interatomic distances in the lattice, arrangement of atoms in the exposed plane, grain boundary and grain sizes of the substrate, and, also, one can include here, defects in the metal catalysts, such as dislocation densities, strains, etc. Electronic factors include the work function and the electronic structure of the substrate (such as the number of unpaired d-electrons in the transition metals and alloys or the d-band character of the metals).

In general, in the study of the catalytic activity one tries to keep all factors constant and vary only one. Often this is difficult to achieve. However, in the case of alloys, one may gradually change one factor, for example, lattice constant, keeping other factors essentially unchanged.

The hydrogen evolution reaction (h.e.r.) has been chosen in this study of catalytic activity since this reaction is simple enough and thus is suitable for the study. Much work has been done on h.e.r. in the past, and its mechanism and rate is known on a number of metals. It has a comparatively high rate of reaction and seems suitable for examining the various factors that will affect the rate.

2. Cell and Solution Preparation

An all glass cell consists of three compartments separated by stopcocks: the test electrode, counter electrode and reference electrode compartment. Experiments were done under highly pure conditions. The cell is cleaned with an $\text{HNO}_3\text{-H}_2\text{SO}_4$ mixture, and then with distilled and conductivity water. The electrolyte was prepared inside the cell without exposure to the atmosphere from the "Transistar" grade H_2SO_4 and redistilled conductivity water. The concentration of the acid is determined by conductance measurements in the counter electrode compartment. During the experiments, pure hydrogen is bubbled through the reference and test electrode compartments, and nitrogen through the counter electrode compartment. Further purification is made by pre-electrolysis.

3. Electrode Preparation

Electrodes in the form of wire ($d \approx 0.5 \text{ mm}$) were sealed in glass tubes, and as far as possible were treated in the same way. Usually, electrodes were cleaned with $\text{HNO}_3\text{-H}_2\text{SO}_4$ (1:1) mixture for a few seconds and then with slightly warm 50% HCl solution. Finally they were washed

with conductivity and redistilled conductivity water. The washed electrodes were heated in a furnace placed above the test electrode compartment at approximately $1/3$ of the melting points of the metal or alloy concerned. They were heated for 2 - 3 minutes in hydrogen, and then for 15 - 30 minutes in a N_2 atmosphere. After being cooled in the N_2 atmosphere, electrodes were transferred into the test electrode compartment without being exposed to the room air.

4. Experimental Procedure and Results

Tafel lines were determined for both cathodic and anodic sides of the reaction. In order to avoid possible oxidation and formation of oxides on the electrode, electrodes were always kept at potentials below those at which oxides may form. It was observed that electrodes which have been anodized for a short period of time (a few seconds) and then reduced behave differently.

Among the noble metals, Pt, Rh, Ir, Pd and Au electrodes have been examined. Also, measurements were made on Au-Pd, Au-Pt and Pt-Rh alloy series. Four compositions of palladium gold alloys, 25, 50, 75 and 90 A+% Pd, have been examined. Three Pt-Rh, and three Pt-Au alloys were available for these experiments. Compositions of these alloys are given in Table I together with the results obtained in this work. Literature results on Ni are also included.

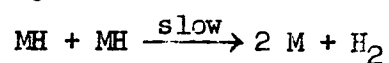
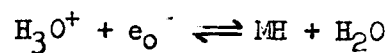
5. Discussion of the Results

Diagnostic criteria for the evaluation of some mechanisms of the hydrogen evolution reaction have been summarized by Bockris.⁶ For

TABIE 1: Exchange Current Density and Tafel b Parameter for Hydrogen Reaction on Various Metals and Alloys (Acid Solutions).

Substrate	i_0	b
Au	5×10^{-5}	110
Pt	10^{-3}	30
Ni ⁶	10^{-5}	110
Pd	10^{-3}	110
Rh	4×10^{-4}	30
Ir	6×10^{-4}	30
Pt-Rh(13%at)	7×10^{-4}	105
Pt-Rh(20%at)	5×10^{-4}	90
Pt-Rh(50%at)	5×10^{-4}	
Au-Pd(25 % at)	7×10^{-5}	110
Au-Pd(50 % at)	7×10^{-5}	105
Au-Pd(75 % at)	2×10^{-4}	110
Au-Pd(90 % at)	5×10^{-4}	115
Au-Pt(10 % at)	5×10^{-5}	110
Au-Pt(20 % at)	6×10^{-5}	110
Au-Pt(95 % at)	5×10^{-4}	30

platinum with a slope, b, of 30 mV, the proposed mechanism includes slow atomic combination:



The mechanism of hydrogen evolution on Rh and Ir electrodes, which show the same slope as platinum, may also include slow atomic combination, but further evidence is required to support this assumption. Slope of about 110 mV obtained on Pd, Au, on Au-Pd alloys and on Au-Pt alloys rich in gold is compatible with a number of mechanisms and as yet it is too early to discuss mechanisms on these metals and alloys. Even so, exchange current densities obtained on these metals and alloys can be analyzed and related to some properties of the substrates.

In Fig. 4 exchange current densities on Au, Pd and Au-Pd alloy electrodes are plotted against the atomic composition of alloys. Three Au-Pt alloys are also included. There is little change, if any, in the catalytic activity on Au and on Au rich alloys for the hydrogen evolution reaction. On the Pd rich side of the Pd-Au system, however, activity appears to be rather sensitive to the change in composition of alloys.

It is possible to plot the experimental values of $\log i_0$ versus the expected number of unpaired d-electrons per atom in these metals and alloys (Fig. 5). The plot reveals that the activity changes linearly with the number of d-electrons, at least to a first approximation. Experimental data on more alloy compositions will be required before a definite conclusion with respect to the exact dependence can be made.

It is significant that Pt-Au alloys which are rich in gold have Tafel slopes close to 120 mV, thus behave differently than Pt. If, on the basis of the identity of slopes, it is assumed that the mechanism of the hydrogen reaction on these alloys is the same as on Au electrodes, then the i_0 values on these alloys may be compared with those obtained

on Pd-Au alloys. From Figures 4 and 5 it appears that the same trend in the change of catalytic activity exists in gold rich Pt-Au alloys as in Pd-Au alloys. What is surprising is that a Pt-Au alloy which is rich in platinum, should follow the same trend, although the Tafel slope for this alloy is different from that observed on Pd or Pd-Au alloys.

A similar dependence of $\log i_0$ on the number of unpaired d-electrons was recently observed on Cu-Ni alloys.⁷ Both of these examples, and the behavior of Pt-Au and Pd-Au alloys, show that the d-electron structure must be considered in the analysis of catalytic activity for the hydrogen reaction. Further study on the catalytic activity on other metals and alloys is in progress with the aim of determining other properties which might affect catalysis.

IV. DEACTIVATION OF ELECTRODES

1. Objective of the Study

The objective of the study is to determine factors causing the activity of an electrode for a given reaction to decrease with time. There may exist a multitude of factors, often aiding each other in causing this deactivation phenomenon. The purpose of the investigation is to find these factors and to evaluate the relative contribution of each in the deactivation in typical cases of electrode kinetics. Understanding the general phenomena has particular bearing in electrocatalysis in fuel cells.

2. Criterion of Deactivation

Under steady state conditions, the current-potential relationship is well defined, and can be measured either galvanostatically or potentiostatically. When deactivation occurs, an electrode begins to show a drift in either potential or current from that of the steady state during the respective conditions of galvanostating or potentiostating. The magnitude of drift is dependent on time, and the changes in current or potential during electrode kinetic studies might constitute a criterion for the deactivation. In the present studies the galvanostatic procedure has been used.

3. Choice of Reaction

The magnitude of deactivation and the causes for the same depend mainly on the kinetic parameters of electrode reaction. Selection of

reactions to study in this work is based mainly on the importance of gas electrode reactions in fuel cells. Two gas electrode reactions have been chosen; these are (i) electrodisolution of oxygen and (ii) oxidation of hydrogen. Commonly used electrode materials, such as platinum, silver and nickel, have been considered. The choice of the electrode system would depend on the conditions of the experiment, namely on the acidity or alkalinity of solution and on the potential range for the experiment. In the reporting period preliminary experiments have been carried out on the oxygen reduction reaction on platinum electrodes.

4. Possible Causes of Deactivation and Experimental Planning

There are two general views which may explain the phenomenon of deactivation. One of these is poisoning theory, and the other is the theory of "recrystallization," or rearrangement of the electrode surface. The former refers to the effect in which adsorption and accumulation of impurity on the electrode (and also in the solution) causes the deactivation. The "recrystallization" view relates the deactivation to the intrinsic change in the electrode surface that occurs during the reaction time.

Investigation of the phenomenon of "recrystallization" obviously calls for optical examination of the electrode surface before, during and after the reaction. Both light and electron microscopic studies have been planned in this regard. The general difficulty one experiences during these measurements is the preparation of flat surfaces required for the microscopy. In these experiments, platinum electrodes were made by sputtering on flat glass. Sputtered electrodes have fine

micro-crystalline structure under high strain, and as such are prone to deactivate by recrystallization. This type of deactivation may be discriminated from that due to "poisoning" by comparing experimental potential-time curves obtained with the same electrode in two fresh solutions.

The poisoning theory may involve many possibilities, ranging from the formation of a visible "passive" layer that blocks the electrode, surface to that of the attack of a small amount of "poisons," which may be the products of the reaction, at active centers. Due to their participation in the electrode reaction, "poison" may also cause mixed potentials to establish. The influence of this type of deactivation depends mainly on the sources of "poisons" and the rates at which they are introduced into the reaction system. Very low concentrations of these substances could cause deactivation, and thus present analytical problems in their detection and determination. An indirect approach to this problem could be made by comparing the high purity runs with those done under normal conditions, and those run in the presence of "impurities" at known concentrations. Spectrophotometry, gas chromatography, gas absorption technique, and mass spectroscopic methods can be used in the analysis.

5. Experimental Procedure

5.1 Chemicals and solution

Analytical grade chemicals are used to prepare solutions. Further purification is rendered by pre-electrolysis. The gases used in the studies are also purified by passing through purification trains.

Between the purification train and the main cell was placed an auxiliary vessel containing redistilled conductivity water. It served to saturate the gas coming out of the purification train with water vapor. In this way discharge in the solution concentration in the main vessel was avoided. Since the effect of deactivation is that of negative catalysis, the "history of the electrode" is controlled by using a new electrode, prepared in the same way, for each measurement. Sputtering technique affords preparation of the electrode a few hours before it is intended to be used. By careful transfer of the electrode in special containers, the effect of contamination has been minimized.

5.2 Electrodes

Initial sputtering experiments showed that opaque films of platinum are non-adherent to glass in spite of careful cleaning of the glass surface. In order to overcome this difficulty, a thin film of tantalum (a few angstroms thick) is first sputtered on glass, and then a thick coating of platinum is applied. With this technique a well adherent film of platinum is obtained. The base layer of tantalum does in no way interfere with the performance of platinum electrode, as the platinum layer is non-porous. Also, there is no edge effect as tantalum oxide, to which tantalum transforms, has sufficiently high resistance (an insulator), and does not take part in local cell reactions. In order to get the suitable shape of sputtered electrode, a die was designed and made. It has provisions which prevent spreading of the sputtered material to the edges of the supporting glass that give the exact size of the electrode and, at the same time, allow a narrow extension for making the contacts fit. To mount the electrode

in the cell the contact end of the slide is held in position with a thin platinum foil and a Teflon clip. Electrical connection is made to the thin platinum foil by a platinum wire which is sealed to the glass tubing and attached to the cell cap.

5.3 Circuitry

Due to the time required for each experiment (about one week), and the need to have a number of experiments so that the results can be statistically calculated, experiments were planned to run in six cells simultaneously. In order to use only one vacuum tube voltmeter, one constant current source, and one recorder for measuring in all cells, a cam switch had to be introduced in the circuit. It allowed alternating measurements to be made on the different cells. The current flowing through each cell was kept constant and the potentials of the electrodes in the individual cell were measured and recorded independently.

6. Data and Discussion

In the preliminary measurements, the variation of potentials with time on platinum electrodes in oxygenated sulfuric acid solutions was followed. Current density on each electrode was different. Fig. 6 gives the long time polarization curves for the different current densities.

Data on open circuit potentials of the systems before and after the long time polarization studies has also been collected. It has been found that the rest potential on an electrode after long time polarization is 60 to 80 mv less than that before it was subjected to polarization. A fresh electrode immersed in the solution already used for long time

polarization shows the rest potential in between that of the fresh system and of an electrode after prolonged polarization. Further, an electrode already used for polarization measurements, when dipped into fresh solution takes up rest potentials in between fresh and polarized systems.

As a first approximation, it can be assumed that at any instant an electrode is in quasi-equilibrium with various components affecting the electrode kinetics, and that a pseudo-steady state is reached. With this assumption, a set of Tafel lines, each for a given interval of time, could be drawn from the current-potential relationship. This is shown in Figure 7. The following conclusions can be drawn from such a plot:

(a) The slopes of all the lines are around 80 mv of the time to which a given line corresponds. This indicates that the same electrokinetic mechanism is involved all through the reaction, from 8 sec to 50 hours of polarization.

(b) On extrapolating the Tafel lines to the potential of reversible oxygen electrode, i.e. 1.23 V, the exchange current density for different intervals of time can be calculated. In the following table, the variation of exchange current density with time of deactivation are given (Table II).

It is seen that there is a gradual decrease of exchange current density with increasing time of polarization. The cause of deactivation of the observed magnitude may be due either to intrinsic change in surface structure and area of the electrode, due for instance to rearrangement in the surface, or due to "poisoning." Rest potential

TABIE II. Extrapolated Exchange Current Densities at Various Times of Polarization

Time of deactivation	Exchange current density amps/cm ²
8 sec.	2.1×10^{-11}
1 min.	1.3×10^{-11}
1 hour	5.5×10^{-12}
10 hours	2.6×10^{-12}
50 hours	1.4×10^{-12}

measurements are indicative of the predominance of the latter cause. Further diagnostic experiments are, however, required to find out the relative contribution of the above mentioned causes of deactivation.

V. MODEL POROUS ELECTRODE

A. DESIGN OF POTENTIOSTAT

1. Introduction

The "slit" electrode can be studied in either of two modes, i.e. constant current or voltage (and related transient forms). Each mode yields useful information. With constant current, one has accurate knowledge of the number of coulombs passed, but the potential usually swings through a wide range, where several reactions are possible (and not controllable in many cases). Steady state values are frequently reached only slowly, for double layer and pseudocapacitance charging must be accomplished before the reaction under study is affected. The constant current mode has the advantage that IR drops, while they may be large, are relatively constant and can easily be calculated out (except where IR changes associated with diffusion controlled concentration changes in the electrolyte are concerned.) Consecutive reaction steps are usually fairly well defined, and the amount of reaction can be simply determined.

Potentiostatic measurements have the advantage that at least in simple systems, only one reaction predominates at a time, and that system can be isolated and studied by a judicious choice of potential interval.

The interpretation of the resulting current measurements are relatively straight-forward for the steady state, but transients present difficulties arising from several sources.

a. Since the current can vary over several orders of magnitude

with time, the IR drop is not constant, and the assumption that the "true" electrode potential is reached almost immediately is frequently quite incorrect.

b. Potentiostats, being high-gain wide band-width feedback devices, with a relatively fixed gain-band width product, have a resultant inherent limitation as to the response time and/or the voltage accuracy obtainable. In order to optimize this behavior, correct cell design can be a critical factor for the elimination of oscillation and ringing.

c. IR contributions are not immediately separable, as they are under constant current conditions.

d. With potentiostatic transients, the reaction times may not be selected independently.

Within these limitations, however, potentiostatic measurements are extremely useful. To this end, the potentiostatic circuit described below has been constructed for use with the model slit-pore electrode.

2. Potentiostat

The basic electronic feedback circuit is shown in Fig. 8. A is a high-gain wideband differential amplifier. This amplifier compares electronically the potential difference between the reference electrode (R.E.) and the working electrode (W.E.) (i.e. with respect to ground) to a present potential at E_{ref} . The feedback connections are such that if the measured voltage is too low, the output voltage is raised sufficiently to increase the current through the auxiliary electrode, and to bring the potential back to the desired value. A similar

but opposite action occurs if the voltage is too high.

In actual practice, the situation is more complex than as stated above. The gain of the amplifier is limited by the following considerations:

a. The more stages present in a D.C. coupled feedback amplifier, the greater will be the internal phase shift at the frequency extremes, and the greater the likelihood of oscillation.

b. Drift and noise, both inherent parameters of the input stages, are amplified as well as the input error signal, and amplification beyond the point where the signal and noise are approximately equal is clearly of no value. These and other inherent limitations can be roughly, but conveniently, expressed in terms of a "gain-bandwidth product." For a given system, this means that voltage accuracy can be obtained only at the expense of transient response and vice versa.

The potentiostat used in the present experiments is shown schematically in Fig. 9. The amplifier is channel one of a Tektronix Type 3A3 dual-trace differential preamplifier in a Tektronix Type 564 Storage Oscilloscope. (Note: in this series of oscilloscopes, the D-C coupled, ground referenced signal is available at pins 11 and 12 of the preamp connector and may be brought out through jacks in the rear of the unit.) Also included is an output compound emitter-follower amplifier consisting of 2N1132 and 2N1906 transistors which form a low impedance, high current output for the amplifier. The output of the oscilloscope has a $\pm 15V$ swing, and resistors R_1 and R_2 serve to limit the current drive into this stage. (Since only the anodic region is to be studied, PNP transistors were chosen for the output. If cathodic measurements were

to be performed, NPN units such as the 2N2053 and 2N2054 could have been substituted with reversed polarities.) Use of the oscilloscope preamplifier, with its variable gain control allows the selection of optimum gain consistent with oscillation-free operation.

Two potential reference sources are incorporated in the unit. One is Zener diode referenced by back to back Zener diodes D_1 and D_2 with respect to ground, and is used for setting the base-line steady-state potentials for the transients. Switch S_4 selects the polarity of current through the Zeners by way of the current limiting resistor R_8 . Approximately 6 volts is developed across the diodes, and R_5 trims the resistance of the string $R_{4,5,6}$ & 7 such that precisely 1 ma flows through. R_4 and R_7 are precision 1K resistors, selected by switch S_3 such that only one at a time is in the string, producing a one volt drop above or below the 10-turn pot R_6 . In this fashion, ten turns of the pot R_6 can be set to precisely one volt, and switch S_3 adds an additional volt when needed, giving a base-line voltage from - 2V to + 2V with a resolution of 1 mv.

The second voltage reference consists of a Hg cell B_1 , a 10 K 10-turn pot R_{10} and a trimming resistor R_9 that is used to set the voltage across pot R_{10} to exactly 1 volt. Switching of this auxiliary potential in and out of the circuit is accomplished with the Hg relay K_1 , which is connected so that the battery circuit is normally open (resulting in a longer battery life). When the relay closes, the contacts 2, 3, and 4 are shorted together, giving the current in the pot (which has a relatively poor frequency characteristic) time to build up to a steady value. After about a millisecond, terminal 4 is opened and

the new potential is added (or subtracted) to the base-line value set on pot R_6 . (The rise-time of the voltage reference signal with this arrangement is better than 10^{-6} seconds to within 3% of the final value.) The current through the cell is measured across resistor R_{11} . The rapid transient portion of the current waveform is measured differentially with channel 2 of the 3A3 preamplifier, and observed directly on the oscilloscope screen. The slower portion is measured by the unity gain, DC coupled differential amplifier consisting of a Philbrick P-2 and $R_{12,13,14}$ & 15 which gives a single ended output for driving a potentiometer recorder. (R_{16} and R_{17} comprise an attenuator for setting the recorder sensitivity.)

The auxiliary electrode is then connected to output and the working electrode to ground. R_3 serves to bias the output stage in the cathodic direction and draws a standby current of about 30 mA, which current can polarize in the cathodic direction when the output is in a cut off condition. Decreasing the value of this resistor will increase the maximum cathodic current, but at the expense of the anodic branch.

3. Error Analysis

A possible equivalent circuit for an electrode system under study is shown in Fig. 10.

The potentiostat amplifier is shown at A_1 , the current amplifier is A_2 . R_A and C_A represent the auxiliary electrode, R_{cell} is the solution and/or stopcock resistance between the auxiliary electrode (A.E.) and the point of connection of the reference electrode capillary (which has a resistance R_{cap}). The working electrode comprises R_R (the equiv.

reaction resistance), C_{DL} (the double layer capacitance), and R_{PS} and C_{PS} (the resistance and capacitance associated with any pseudo capacitance).

Distinction must be made between the "true" electrode potential and the potential held constant at the tip of the capillary. At steady state values where the current has dropped to the milli- or micro-amp range this form of error is not serious. However, during the initial portion of a transient, when the current can be several hundred mA, the C_{DL} prevents the electrode potential from changing instantaneously and all of the voltage change is present as IR drop across R_{soln} (solution resistance). Even at steady state there is still an error voltage δE at the tip of the capillary given approximately by

$$\delta E_{reg} = \frac{i(R_m + R_A + R_{cell} + R_{soln} + R_R)}{A}$$

With a typical amplifier gain, A , of 1000, at high currents, of the order of 100 mA, even moderate resistance ($\sim 100 \Omega$) in any of the components can produce errors of 10 mV. The "true" electrode potential, η , will be off by yet another factor

$$\delta \eta = \delta E_{reg} + iR_{soln}$$

Associated with any system for measuring the current will be the stray capacities C_1 and C_2 . These capacities will not directly affect the accuracy of the transient potentials at the electrode, but they do create problems in the measurement of the current. If C_1 is large, it can produce unwanted phase shift in the feedback loop, leading to increase instability and oscillations. C_2 will also introduce its own phase shift, but it has the additional drawback that all current needed

to charge it to a new potential also passes through R_m , the current measuring resistor. Thus, even though the voltage may be correct, a spurious current reading can result.

For adequate transient work, the reference electrode and capillary should be designed as carefully as possible, for the capillary and its resistance and stray capacities introduce additional phase shift.

(Note: marginally unstable systems can sometimes be stabilized with a small capacitor between the output and the negative input. This capacitor can take the form of a short section of insulated wire (1-2 ft.) cut in half and twisted together.)

B. EXPERIMENT AND RESULTS

1. Slit Electrode System

Work with the cell described in the previous report⁸ has been started, using the larger slit widths. Fig. 11 shows the steady-state values of current versus potential for three meniscus configurations. Curve 1a is for a slit 5 mm wide, and 1 cm deep in the ascending voltage region and 1b is for decreasing voltages. Curve 2a is for a slit 0.5 mm wide and 2 cm deep and curve 2b is for a slit 0.5 mm wide and 0.5 cm deep. Curve 1a shows an initial rapid rise of current to a diffusion (and convection) limited plateau, and then a rise in current at oxygen evolution potentials. The retrace curve, 1b shows the typical behavior of an H_2 consumption electrode, in that it has become "activated" by the treatment at high anodic potentials.

Curves 2a and 2b, where diffusion and convection are much more

limited, show a lower initial current, and a pseudo-ohmic behavior up to the point of O_2 evolution. These smaller slit sizes also show a marked "activation," but to a lesser degree than in the wide slit case.

Fig. 12 shows two successive runs, with increasing and decreasing potentials, on a slit 0.5 mm x 1 cm. After the initial rising portion 1, the curves were reasonably reproducible and show several regions of interest. (Note: Since potentials were measured vs the Ag-PdH electrode, open circuit is at $E = -0.065$ volts). The first 50 to 100 mV shows the rapid non-linear rise to the diffusion region, after which the current rises more slowly in a linear fashion to about 500 mV. The currents measured in this region are steady and reproducible. Starting at about 500 mV, the current measurements become very erratic and a "mean" value is more difficult to obtain. However, in general, the behavior continues roughly similarly to the first region. In the third region, from 0.9 to 1.6 volts, a negative resistance is encountered, producing low frequency oscillations with a period of 2 - 10 minutes. The cross-hatched areas of the curve represent the range of current excursions during the oscillation. On switching on the potential, the current initially rises to its high value, then slowly drops to the low value (which appears to be a critical current density, relatively independent of potential) and rises again in 2 - 3 seconds to the high value. (The oscillations are probably due to two competing reactions coupled through a mutual dependence on coverage by some species such as oxide, oxygen, etc., on the surface.) Beyond 1.6 volts, visible oxygen bubbles form on the electrode surface, which impede further study; thus, practice is to keep the potential below this value.

2. Meniscus Heating Effect

Microscopic examination of the meniscus during operation of the electrode in the potential region above 0.5 volts showed an unusual behavior. The gas-solution-electrode boundary, previously stable with regard to its position was observed to undergo shifting. Close examination showed that small droplets of liquid were forming on the surface of the electrode in the gas phase, growing in size and moving downward to join the main liquid. This was clearly the cause of the erratic current readings obtained in this region, since most of the current is produced in the meniscus at these potentials, and the actual length of the meniscus probably fluctuates some 10 - 20% locally during the process of drop impingement.

In the anodic consumption of H_2 , the lost energy, which is the product of the current and the overpotential, appears as heat. Considering the immersed electrode as a whole, this dissipation is only a few hundred microwatts per cm^2 . However, since there is good evidence that the current is concentrated in a few tenths of a millimeter (or less) of the meniscus, it is clear that local heating effects can become significant. The probable interpretation of the mobile meniscus is, then, that the local heating raises the temperature of the thin electrolyte film to the point where the vapor pressure of the sulfuric acid solution is equal to the vapor pressure of pure H_2O at the ambient temperature. At this point, a third phase, pure water, becomes stable, and can condense on the cooler electrode above the meniscus. The fact that this behavior has not been observed before, is probably due to the fact that earlier measurements were made in open systems where the H_2O vapor concentration

could never build up to the levels required.

The implications of this phenomenon are interesting from the point of view of real fuel cells. The meniscus heating effects are greater in finer electrode capillaries, and the condensation products above certain power levels can condense in the small capillaries, effectively blocking and/or flooding portions of the electrode from further activity. Also in the absence of stirring in fine pores, a continuous separation of water with resulting high local electrolyte resistance may occur.

VI. NATURE OF THE CATALYST SURFACE

1. Introduction

The rate of an electrochemical reaction may depend on the number of variables which characterize the catalyst surface, for example, the metallurgical grain structure of the electrode.

In the first stage of this project, an attempt has been made to find out whether the grain size of inert metal electrode has an influence on the rate of an electrochemical reaction. Platinum was chosen as the electrode material.

2. Experimental

Platinum electrodes with different grain sizes were prepared by heating at a high temperature, 1650°C or 1250°C. The starting material was a platinum sheet, 0.05 mm thickness. As is known from the literature, the thickness of a metal sheet limits the diameter of grains because the free surface is an inhibitor for grain growth. The maximum grain size obtained from a given sheet was approximately equal to the thickness of the Pt sheet. To get larger grains, it was necessary to take a Pt rod. Grain size was determined by observation under a microscope (see Fig. 13). For the electrode specimens prepared in a furnace, it was observed that the surface was thermally etched with well-revealed grain boundaries. In the case of electrodes not prepared by heating (for instance, the starting material), etching was done by a.c. polarization in an HCl + NaCl solution.⁹

Electrodes were cleaned in hot alkali solution (at 65 - 70°C)

for 1 min., and in a fresh, hot mixture of $\text{HNO}_3 + \text{H}_2\text{SO}_4$ for 1 hour. Electrodes were not activated before measurements.

The cell for the electrochemical kinetic studies was the standard three compartments cell.

3. Influence of Grain Size on the Kinetics of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ Reaction

Current potential relationship for the reaction



was studied by Gerischer¹⁰ in a linear region from + 4 to - 4 mV, and by Lewartewicz¹¹ and Petrocelli¹² under conditions of mixed activation and diffusion control in a wider region of overvoltages (up to ± 200 mV).

After determining the transition time, it was decided to use galvanostatic transient technique to determine the current-potential relationship under conditions of pure activation control. The reaction was studied at room temperature in the solution: 1 M H_2SO_4 , 10^{-2} M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \times 2\text{H}_2\text{O}$, and 10^{-2} M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \times 6\text{H}_2\text{O}$.

Galvanostatic transients, with pulse duration of $200 \mu\text{sec.}$ and/or 10 msec were photographed with Polaroid camera on the CRO screen. Separate transients ($500 \mu\text{sec.}$ duration, from 8 to 40 mV) were taken for determination of ohmic overvoltage, η_{Ω} .

The mean value of the Tafel slope, in the region studied is 125 mV, the double layer capacity $31 \mu\text{F}/\text{cm}^2$, and exchange current density is $1 \times 10^{-3} \text{ A}/\text{cm}^2$. Typical results obtained are shown in Fig. 14. From the figure, one can notice a difference between first and second measurements. The second measurement is well reproduced by further repeating even after 24 hours. Analysis of the results obtained on

electrodes with various grain sizes indicate that grain size has a negligible influence on the i_0 for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ reaction.

4. Kinetics of Hydrogen Evolution Reaction in Acid Solution

Hydrogen evolution was studied in purified 0.2 M and 1 M H_2SO_4 solutions, on non-activated electrodes.

A. 0.2 M H_2SO_4 Solution

Platinum electrodes used in this work were in the form of rods with grain sizes of about 200μ and 600μ in diameter, and also 'as is' starting material.

For determination of the current-potential relationship, long time (about 1 min.) polarization measurements were made. The region examined was 5×10^{-5} to 2×10^{-3} A/cm². In this region, the mean value of Tafel slope was 115 mV. The exchange current density was 5×10^{-5} A/cm². In these experiments, the solution was pre-electrolyzed for 21 hours at 1 mA/cm². Some of the results obtained are shown in Fig. 15. It is interesting to note that second measurements gave slightly higher values with the same slope.

B. 1 M H_2SO_4 Solution

Electrodes used in this study were cut from Pt sheet 'as is'. An electrode with grain size of about 100μ was prepared by recrystallization. Also a platinum cylinder electrode, diameter 5 mm, was prepared with grains of about 700μ in diameter.

The current-potential relationship was determined by long time

(about 1 min.) polarization measurements. The region examined was 5×10^{-6} to 6×10^{-4} A/cm². In this region, the Tafel slope was found to be 49 mV for all electrodes. The exchange current density was 3×10^{-6} A/cm². In these experiments solution was pre-electrolyzed for 40 hours with 10 mA/cm². It is important to emphasize that in all experiments electrodes were not activated.

The results may be taken to indicate that grain size has little influence on the rate of hydrogen evolution reaction.

Future Work

It is intended to use single crystal Pt electrodes and investigate the influence of crystal face on the kinetics.

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FIG.1 Dependence on potential of the coverage of naphthalene on nickel in O_2 containing solutions of 0.01N $NaClO_4$ (x) and 0.1N $NaClO_4$ (o).
Concentration of naphthalene $5 \times 10^{-5} M l^{-1}$

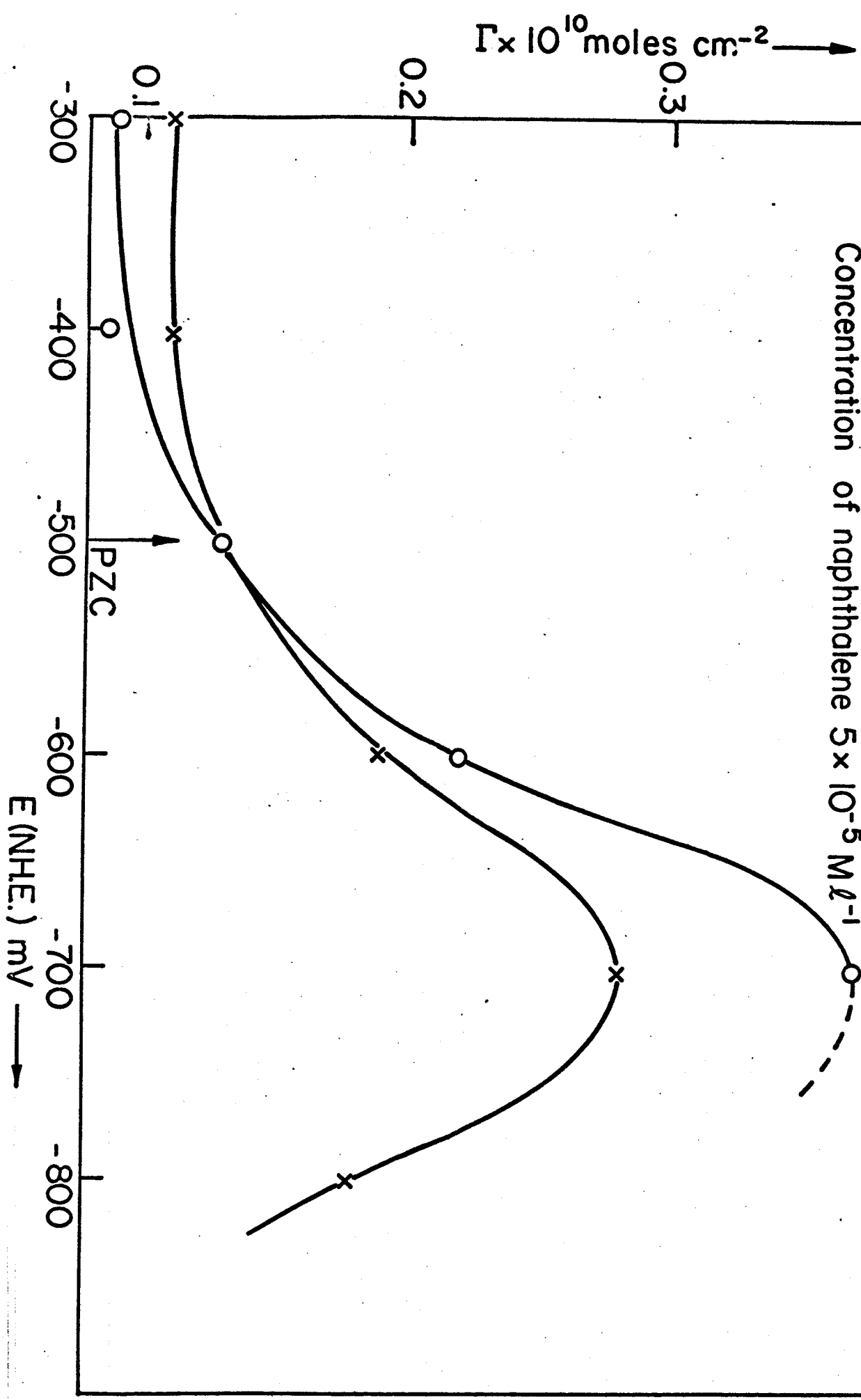
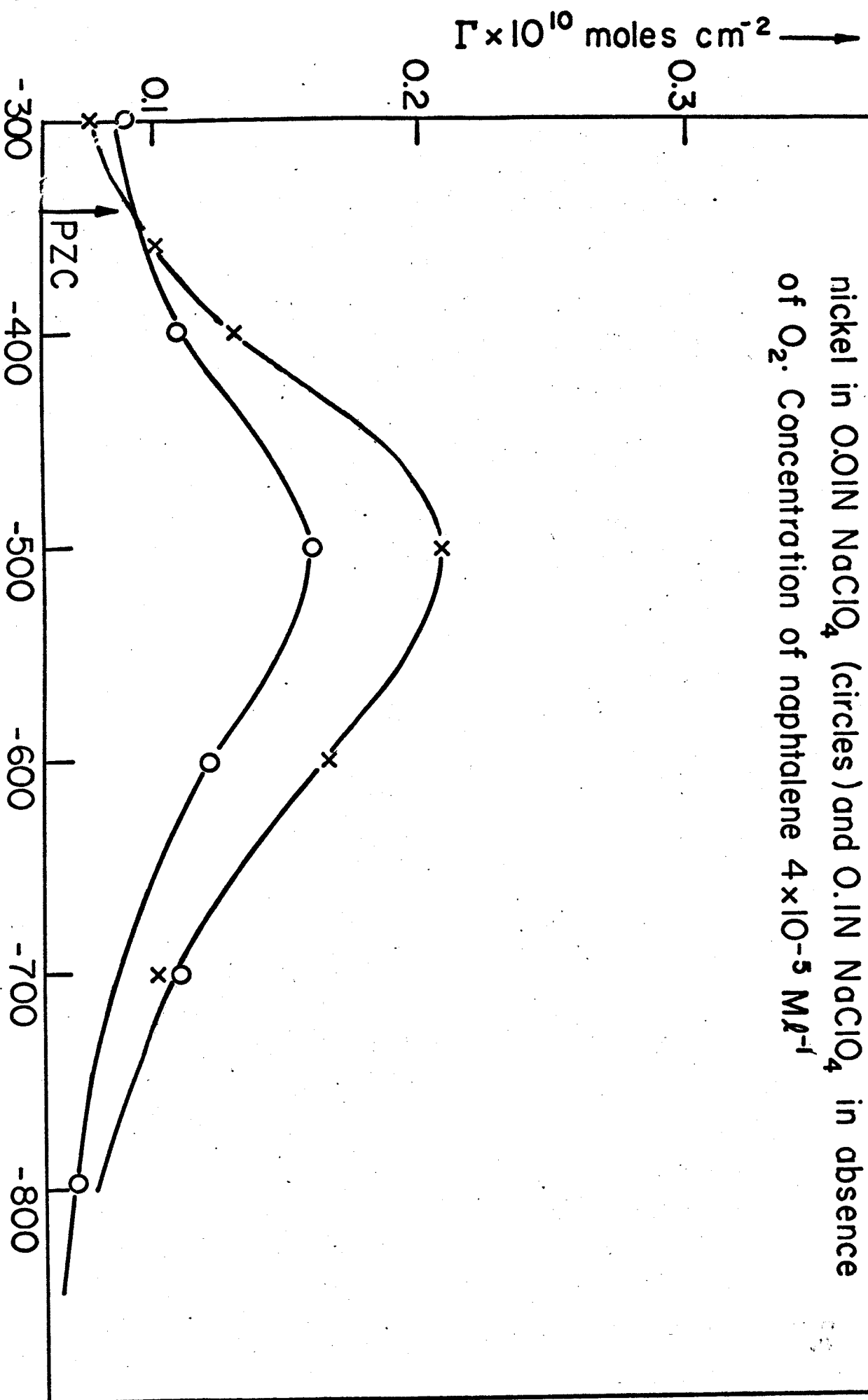


FIG.2 Dependence on potential of the coverage of naphthalene on nickel in 0.01N NaClO_4 (circles) and 0.1N NaClO_4 in absence of O_2 . Concentration of naphthalene $4 \times 10^{-5} \text{ M l}^{-1}$



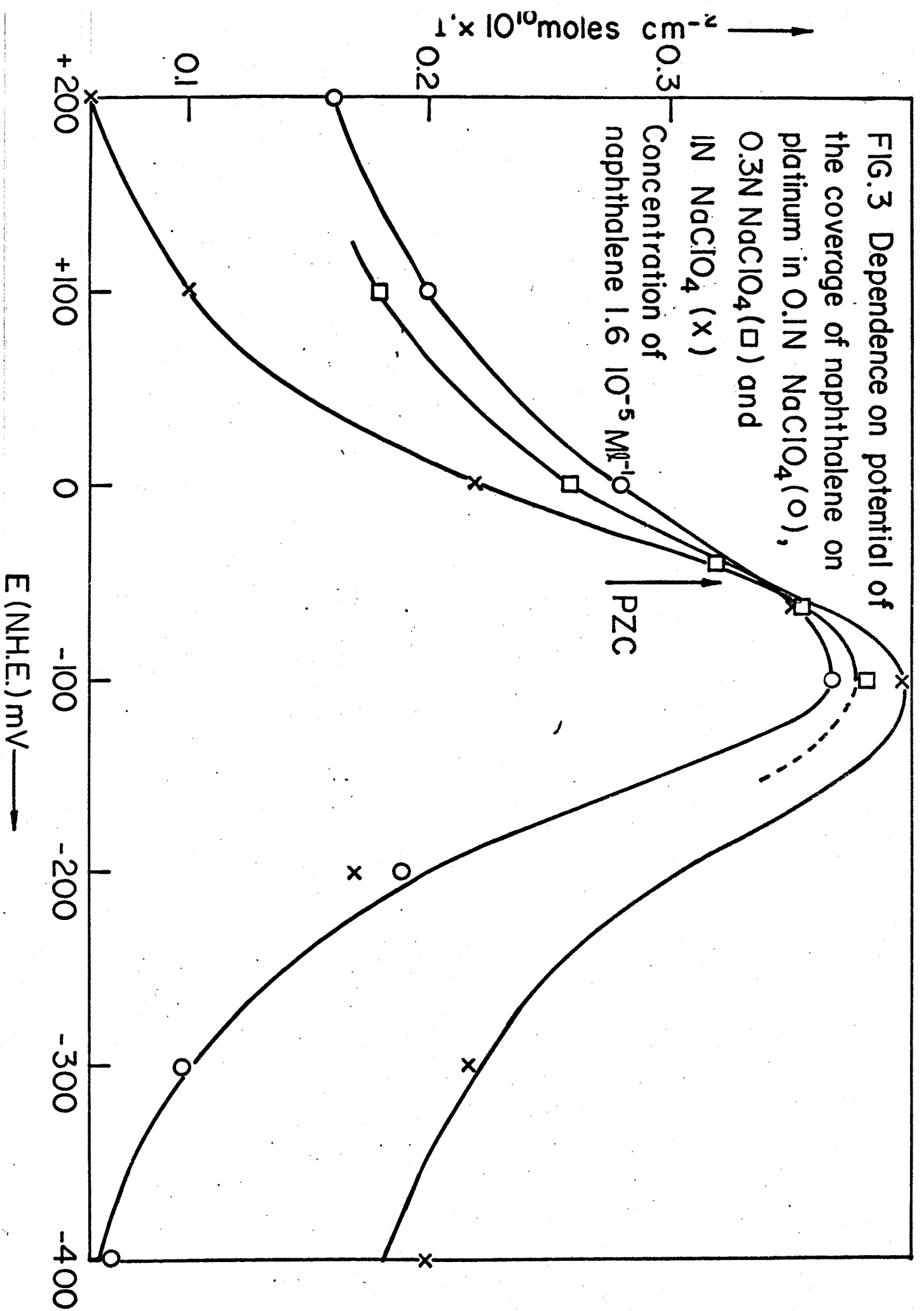


FIG.4 Exchange current densities for hydrogen evolution on Pt,Pd,Au and Pt-Au and Pd-Au alloys.

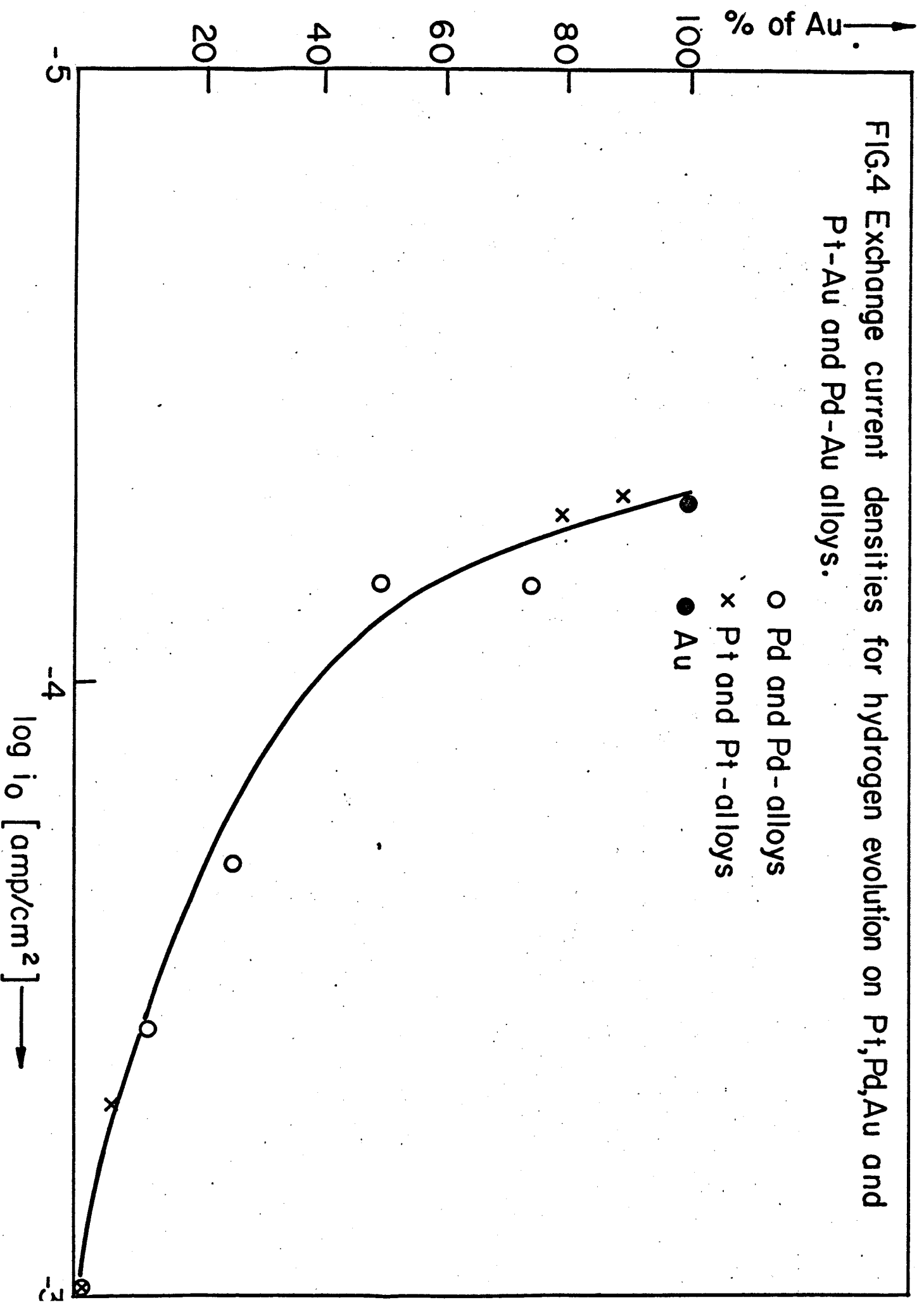
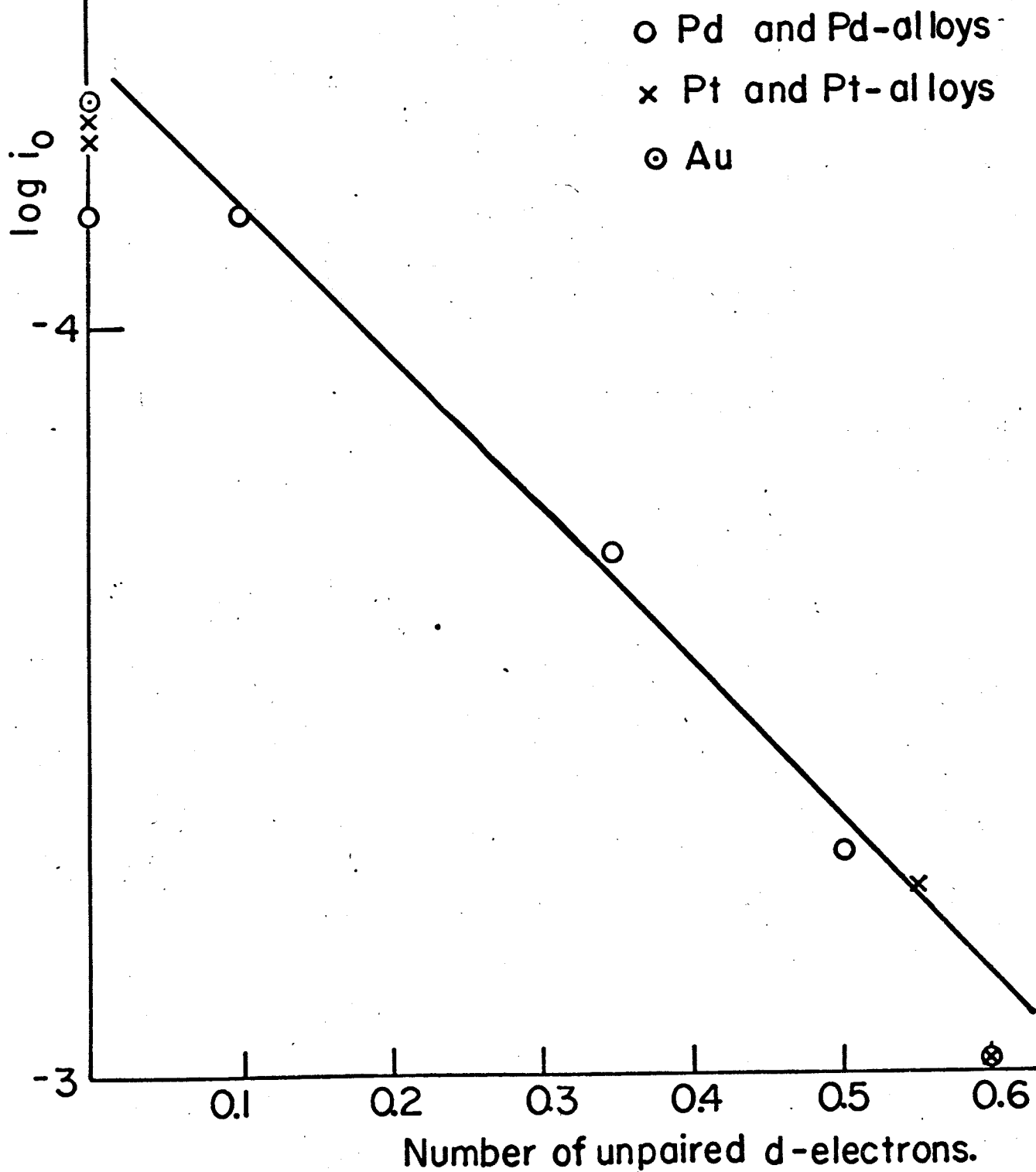


FIG.5 Dependence of $\log i_0$ for hydrogen evolution reaction on number of unpaired d-electrons.



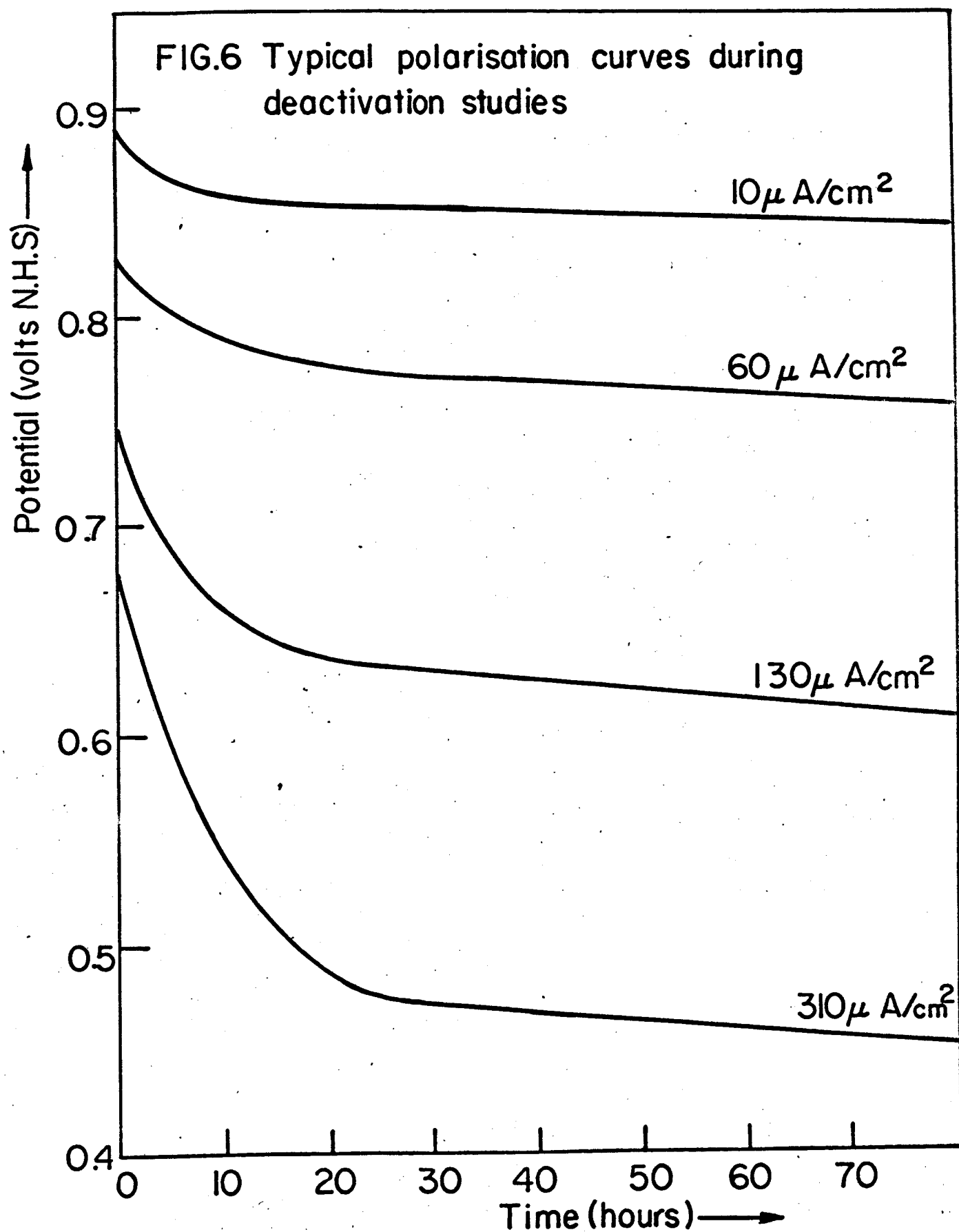


FIG. 7 Tafel lines at different intervals of time

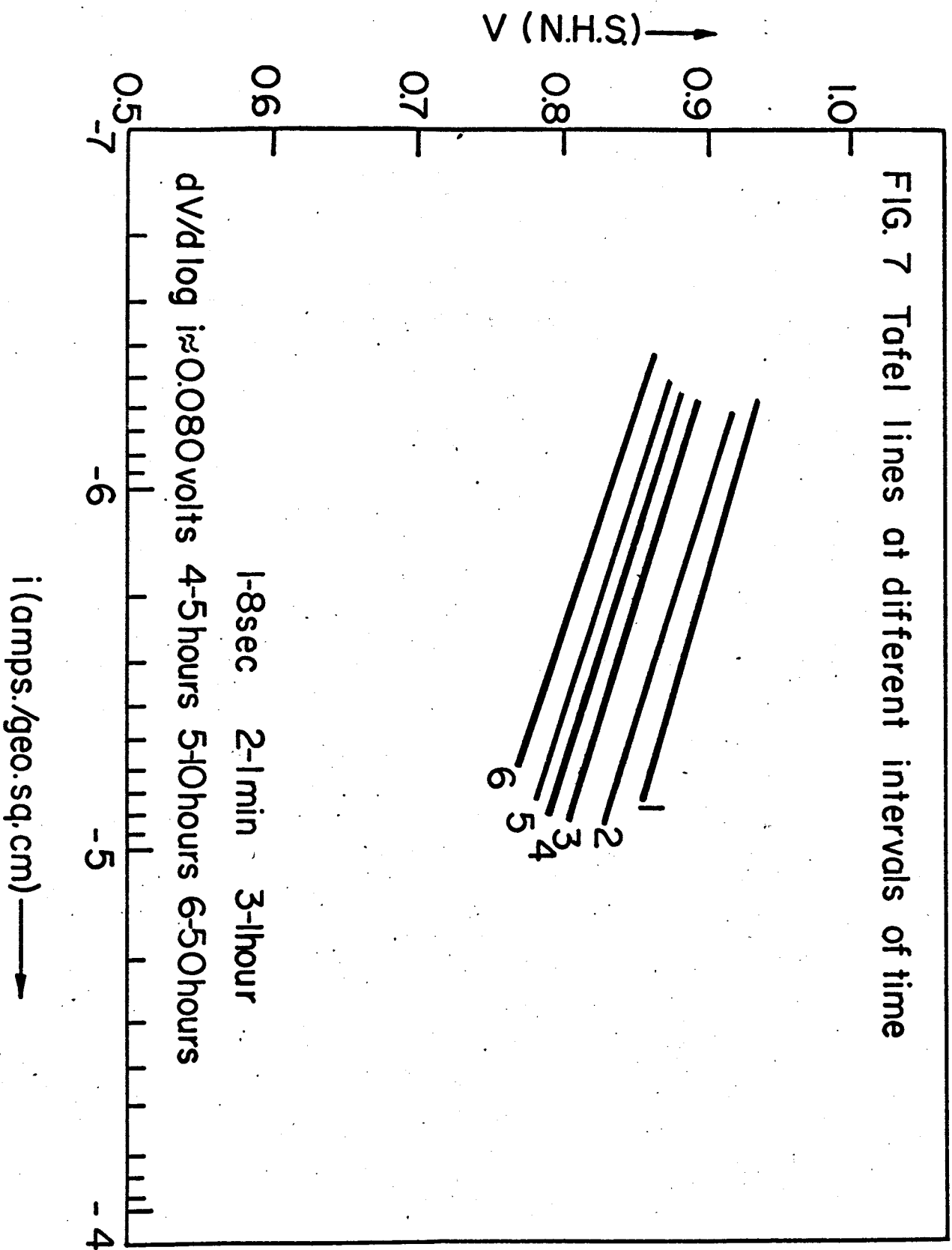


FIG.8 Simplified Circuit for Potentiostat and Cell

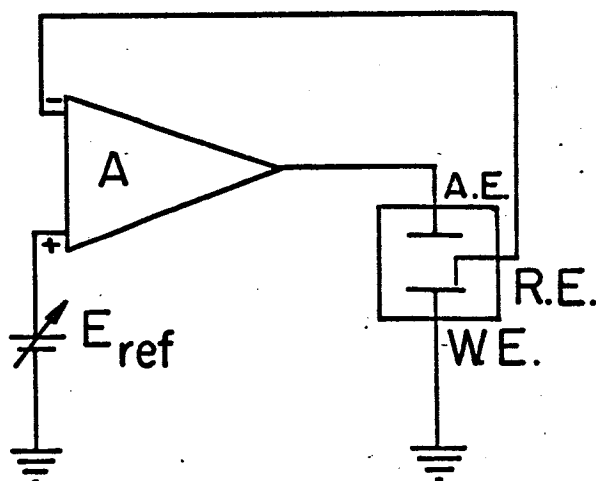


FIG. 9 Complete Schematic for Potentiostat

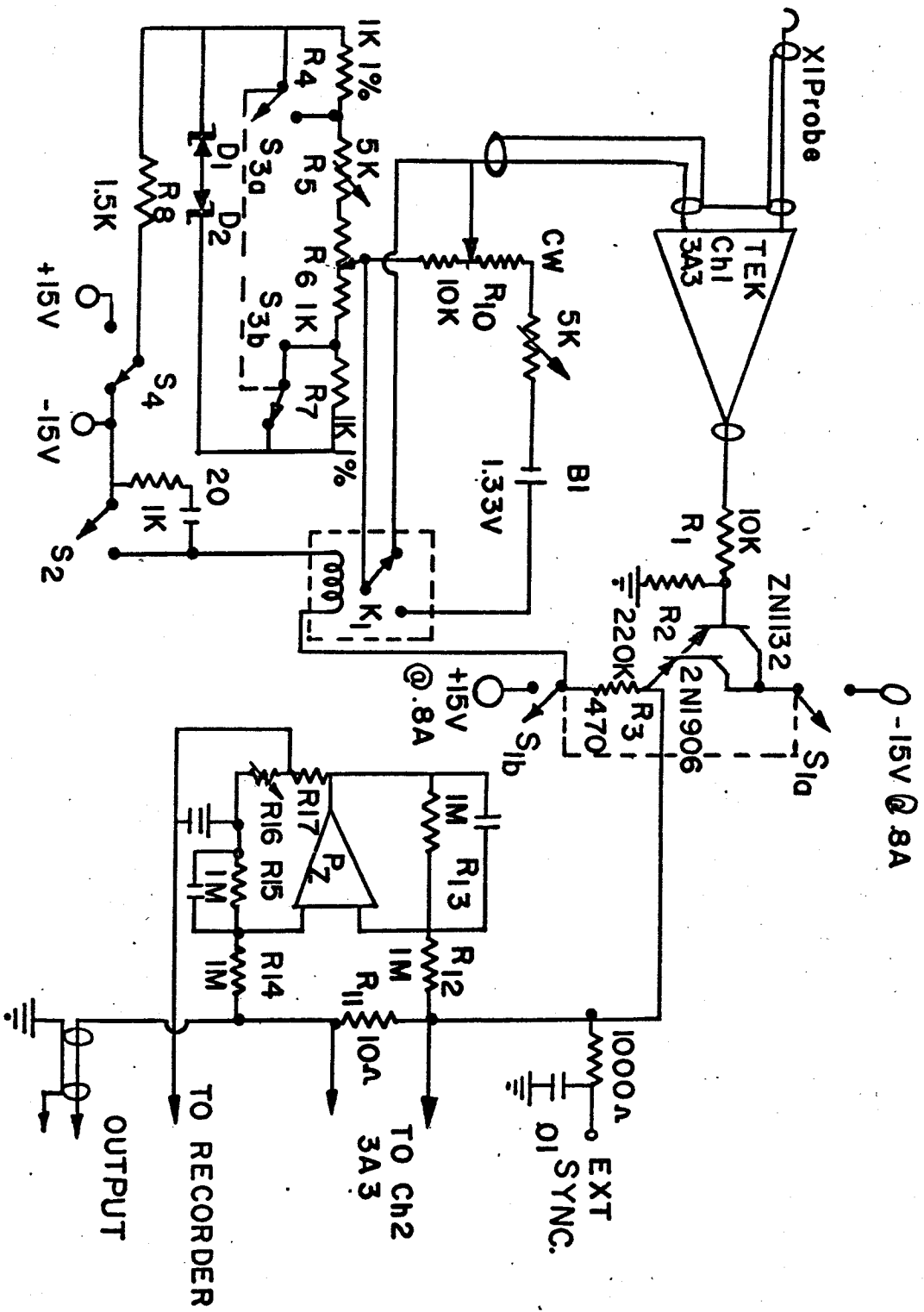


FIG. 11 Typical Current - Voltage Curves for Slot Electrode

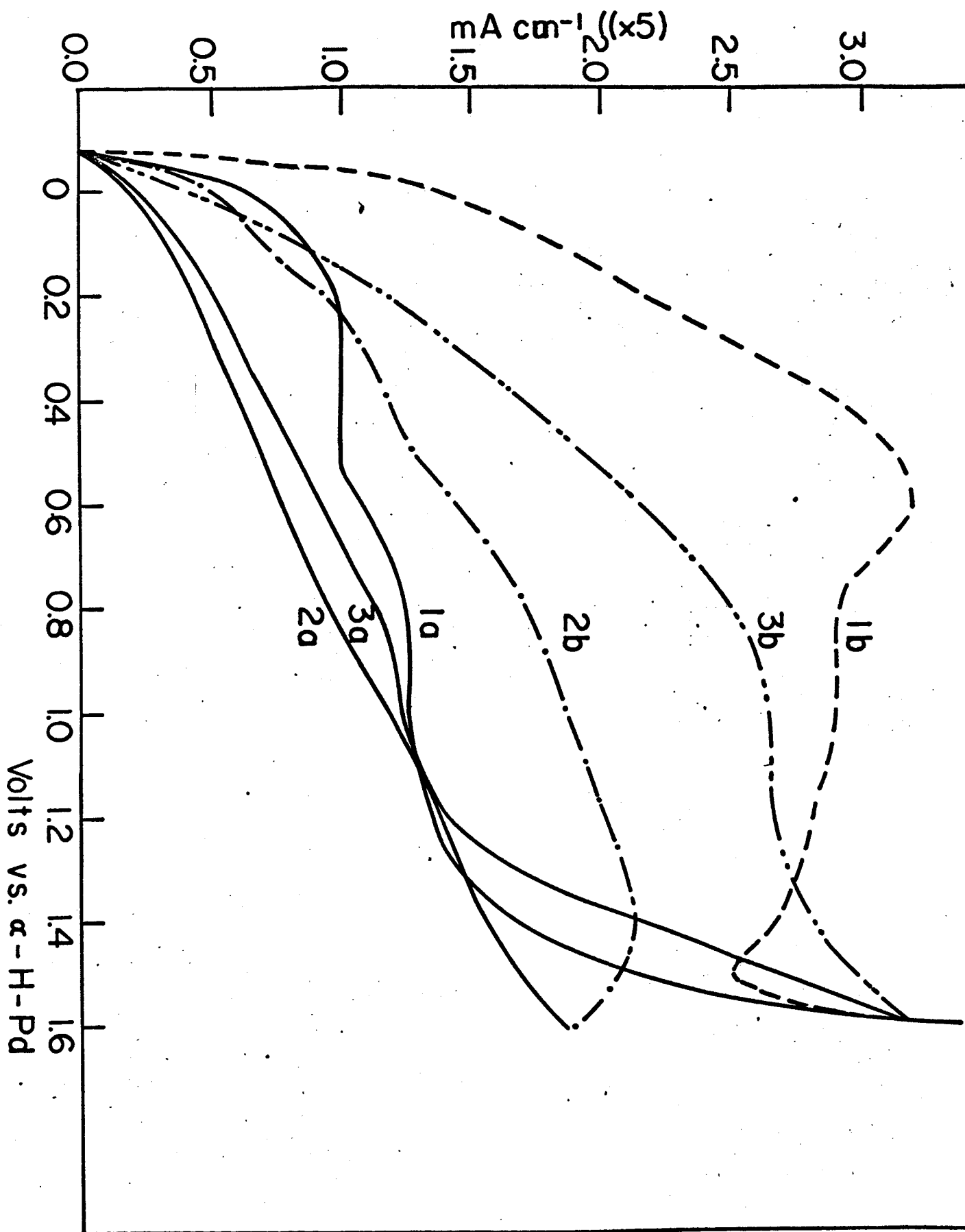


FIG. 12 Current-potential Curves for 0.5 mm Slot Showing Hysteresis

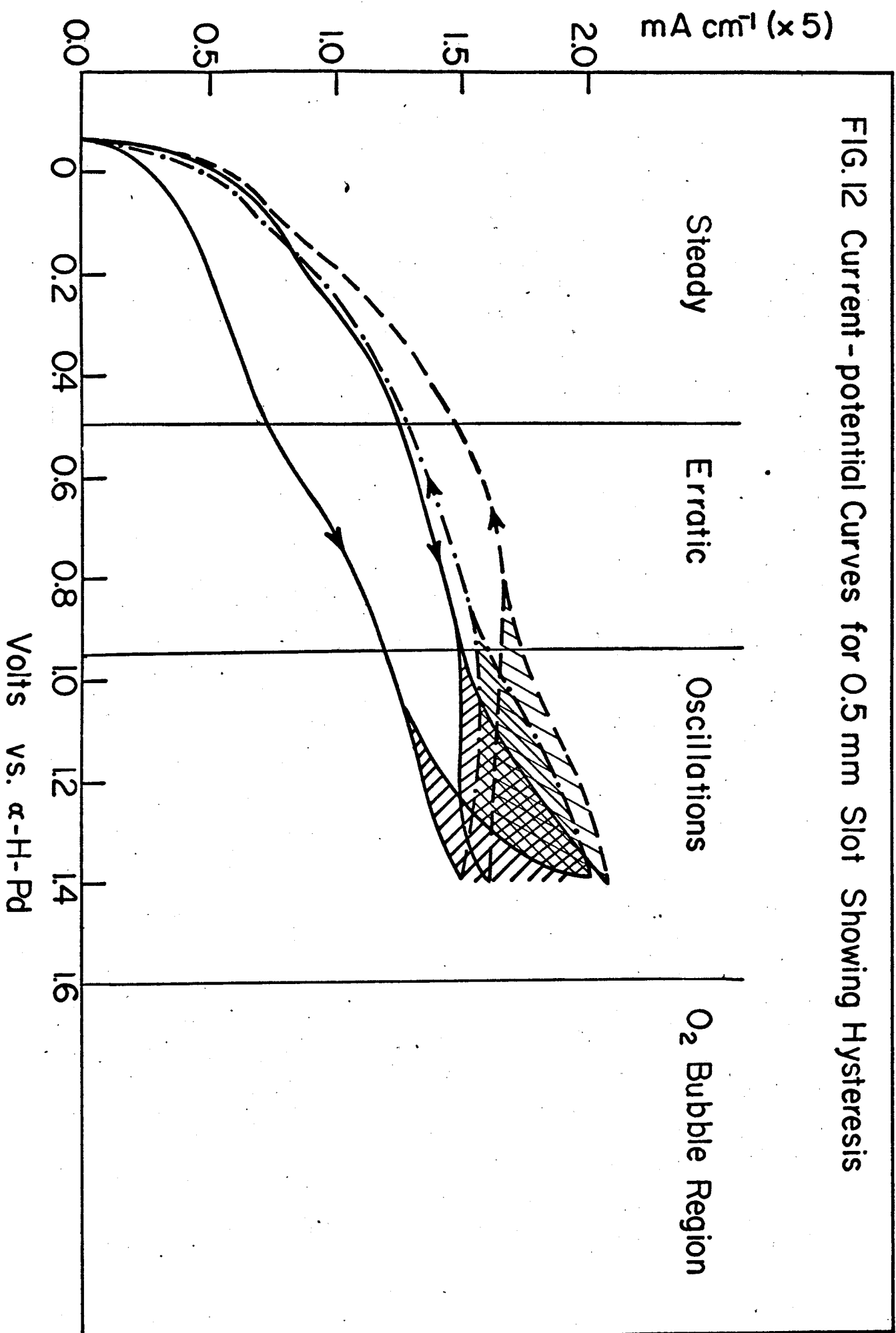


FIGURE 13

Microscopic view of platinum electrode.

Left Figure - magnification 300

Right Figure - magnification 600

FIG. 14 Current-potential relationship for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system.

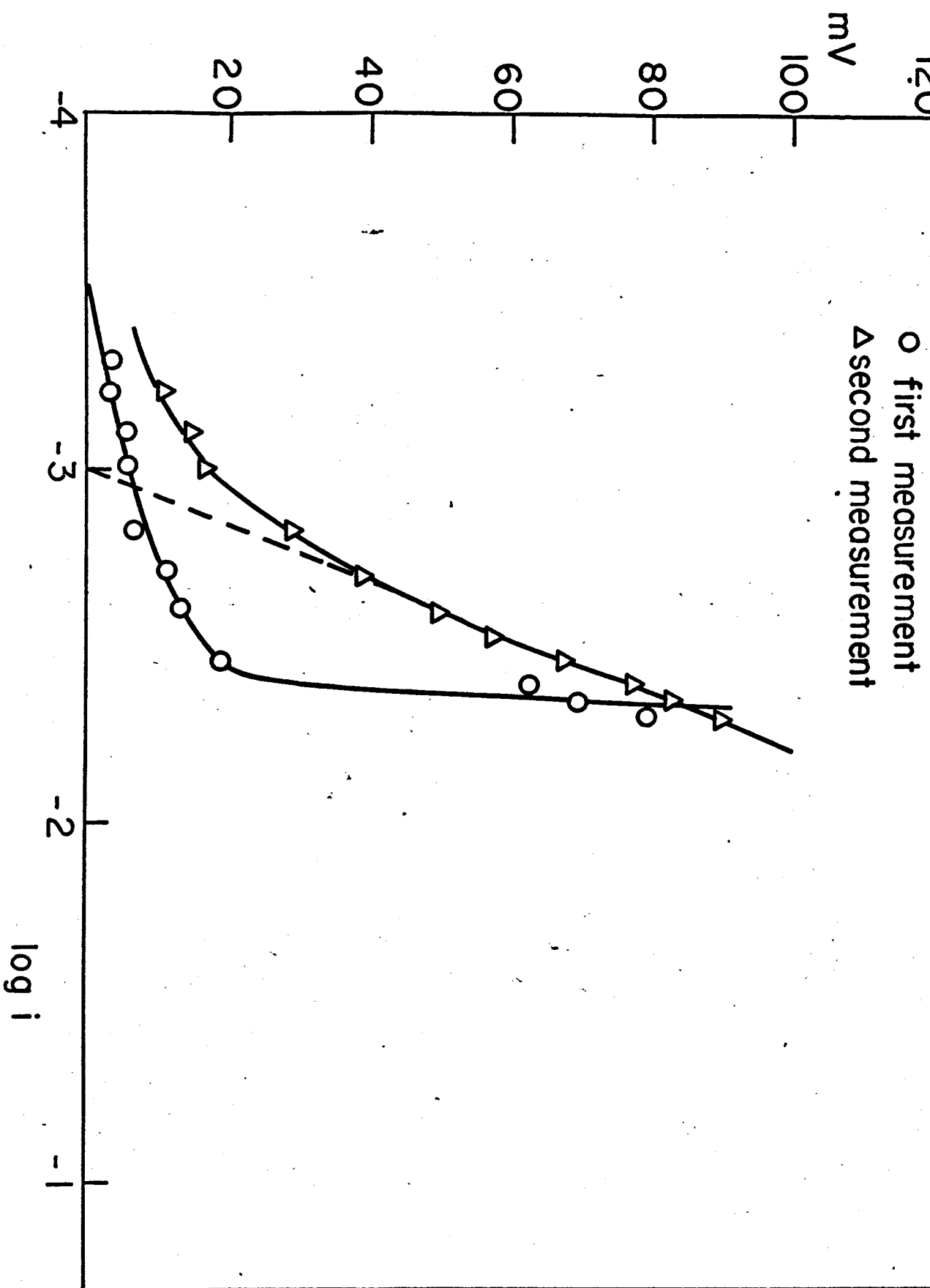
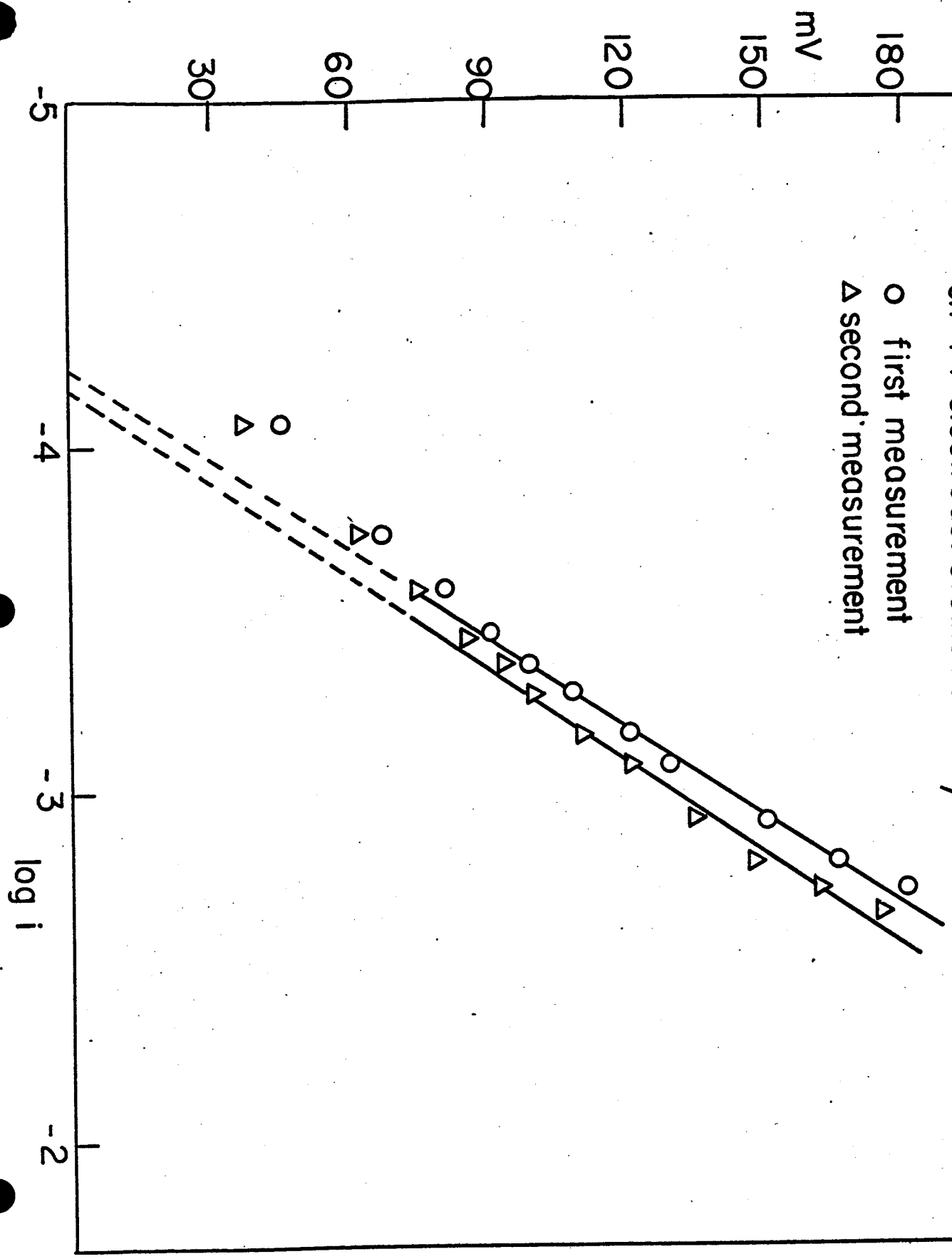


FIG.15 Current-potential relationship for hydrogen evolution on Pt electrode. Grainsize 600μ .



A P P E N D I X 1

ABSTRACT

8
The factors affecting the rates of chemical and electrochemical reactions are discussed. The differences between chemical and electrochemical catalysis arising from the existence of an applied field and from the presence of solvent are discussed from the theoretical and experimental point of view. A discussion of the ways to enhance electrocatalysis is presented.

The mechanisms of several electrode reactions (oxidation of hydrogen, hydrocarbons, oxalic acid, oxygen reduction) pertinent to fuel cell reactions are discussed, as a prerequisite to considerations of catalysis.

An attempt is made to formulate some aspects of the mechanism of catalysis for the hydrogen evolution and hydrocarbon oxidation reactions.

The needed trends in research are discussed.

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ELECTROCHEMICAL CATALYSIS

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I. INTRODUCTION

Among simple divisions which can be made in methods for electrochemical energy conversion, a convenient one is between higher temperature (say $> 300^{\circ}\text{C}$) and lower temperature systems. The aim of working at the higher temperatures is to increase the rate constants of the electrochemical reactions sufficiently so that the overpotentials associated with the interfacial reactions are reduced to negligible amounts. This aim is attained in certain systems, for example in concentration cells in which the interfacial reaction is the dissolution of a metal from an amalgam, and the working temperature is about 300°C (the residual irreversibility is diffusional).³

However, even at 950°C , the overpotential at a c.d. of about 1 amp cm^{-2} for the evolution of CO_2 arising from the discharge of oxyanions in the Al_2O_3 -cryolite system is about 0.7 volts,¹ so that raising the temperature to near to a region above that usually considered practical in electrochemical energy conversion does not necessarily eliminate the need for consideration of factors controlling the rate constants of electrochemical reactions.

For low temperature electrochemical energy conversion, considerable overpotentials exist at the present time in all systems

hitherto devised,³ except that of the hydrogen electrode (see Table I), and this situation particularly in respect to hydrocarbon oxidation and oxygen reduction provides the principal stimulus for studies in electro-catalysis.

Fundamental studies in electro-catalysis have hitherto been few.¹³ Except for those on the hydrogen evolution reaction* (h.e.r.),¹⁴⁻¹⁹ most studies of the mechanism of electrochemical reactions have been limited to one or a very few metals. It may be regarded as premature already to attempt a synthesis of the limited knowledge in the field at present. The central nature of the overpotential reduction (catalytic) problem in electrochemical energy conversion** encourages this attempt. An electrochemical approach to catalysis has importance not only because of electrochemical energy conversion but also because it provides a convenient method of varying the heat of activation for a reaction, and hence inducing controlled changes in its mechanism, a device of great value in catalytic research in general.

The following indicates the possibilities in electrochemical energy conversion, the realization of which depend principally upon improvement of the position in electro-catalysis.

* Thus, the remaining catalytic problems for this reaction are now small.

** This importance increases as the prospects for application of electrochemical energy conversion increase, for the amount of noble metals which would be required for large scale use is too large for the available supply, without increase in the depth of mining and hence of cost.

TABLE I

EXTRINSIC LOSS IN ENERGY CONVERSION EFFICIENCY DUE TO
INADEQUATE CATALYSIS OF REACTIONS CONTROLLING ELECTROCHEMICAL GENERATORS

Electrochemical	T°C	Current Density ₂ (amps cm ²)	Reversible cell poten- tial at T°C	Total over- potential, except IR	Loss in energy conversion efficiency due to inadequate catalysis*
Hg/K-K ³	200°	0.229	1.100	0.182	16.5
H ₂ -O ₂ ²	67°	0.350	1.197	0.515	73.1
H ₂ -Br ₂ ^{4,5}	25°	0.120	1.070	0	0
C ₂ H ₂ -O ₂ ⁶	80°	0.002	1.279	1.100	88.1
C ₂ H ₄ -O ₂ ⁷	65°	0.020	1.167	0.972	80.7
C ₂ H ₆ -O ₂ ⁸	90°	0.028	1.072	0.722	67.2
Decane-O ₂ ⁹	110°	0.073	1.063	0.813	76.5
Methanol-O ₂ ¹⁰	90°	0.050	1.180	0.680	57.6
Urea-O ₂ ¹¹	25°	0.003	1.135	0.735	67.8
Cellulose-O ₂ ¹²	130°	0.002			

*Thus, "adequate catalysis" would be such that, at the current density mentioned, the overpotential would be reduced to the "reversible" region, i.e., say, < 10 mv.

(1): Only three years ago, few chemists anticipated the electrochemical oxidation to CO₂ of a substance as inert as ethane, at temperatures of <100°C.⁸ The complete electrochemical oxidation of cellulose to CO₂ at the same low temperature is perhaps even more surprising.¹²

One is reminded of the ease with which a number of complex biochemical reactions occur at body temperatures with the aid of enzymatic catalysts.²⁰

A good example of electro-catalysis is provided by H permeation into Fe^{21,22} (Table II). Thus, permeation from the gas phase

TABLE II
ELECTRODIC CATALYSIS: THE PERMEATION OF HYDROGEN
INTO IRON MEMBRANE 0.1 cm THICK

Thermal ²¹	Electrochemical ²²
Rate = $A e^{-E_T/RT}$	Rate = $A' e^{-E_E/RT} e^{-VF/RT}$
$A = 3.66 \cdot 10^{-7}$	$A' = 4.2 \cdot 10^{-4}$
$E_T = 9.52 \text{ kcal}$	$E_E = 9.7 \text{ kcal}$
Rate at 600°C: 7.32×10^{-9} moles cm ⁻² sec ⁻¹	$\alpha = 0.25$ in lower, and $\alpha = 0$ in higher potential range
Rate extrapolated to 25°C* for $P_{H_2} = 1 \text{ atm} = 183 \cdot 10^{-13}$ * moles cm ⁻² sec ⁻¹	Rate at 25°C and potential of -.658 V (NHE) in 0.1 N H ₂ SO ₄ = $2.8 \cdot 10^{-10}$ moles cm ⁻² sec ⁻¹ .

*The values of A_T and E_T are those calculated by Sykes et al.²¹ However, Chang and Bennett²³ found that below 400°C the permeation rate of hydrogen through Armco iron falls below that predicted by extrapolation from values found at higher temperatures. The values of permeation found below 400°C varied greatly with the pretreatment of the metal. At these lower temperatures it appears that the surface reactions are rate-determining while at higher temperatures diffusion of hydrogen through the metal is rate-determining. Thus the value calculated for 25°C will be erroneously high.

has to overcome the dissociation of H₂; and H is thereafter adsorbed. Its ingress to the metal is retarded by the dissociation reaction and the strong heat of adsorption of H onto M in the absence of competing

molecules. In the electrodic case, protons from water arrive relatively easily in the surface and the heat of adsorption is reduced¹⁵ by the effect on the M-H bond strength of competitively adsorbing water molecules, so that the heat of activation for permeation is reduced, i.e., the permeation catalysed.

(2): Electrochemical rate constants for the same reaction on different metals have a very wide spread, e.g., some 10^{10} for the hydrogen evolution reaction;²⁴ about 10^5 for the oxygen evolution²⁵ and metal dissolution reactions,²⁶ i.e., the catalytic effects of different substrates are very wide. The value to which it is worthwhile attempting to increase the exchange current density (i_0) is the limiting current density due to mass transport. The order of magnitude of this in amps cm^{-2} , at room temperature in well agitated aqueous solutions is (for reactions at planar surfaces) roughly equal to the solubility of the reactant in moles l^{-1} .

Thus, the value of the exchange c.d. for the oxidation of C_2H_4 to CO_2 on platinized platinum in 1 N H_2SO_4 at 80°C is 10^{-8} .²⁷ The solubility of C_2H_4 at 80° in this solution is $\sim 2 \times 10^{-3}$ moles l^{-1} . Hence, the overpotential for this reaction will remain negligible (energy conversion efficiency near 100%) up to a rate at which the oxidation becomes controlled by mass transport if the exchange current density were increased to about 10^{-3} A cm^{-2} , namely, if the heat of activation were reduced by about 14 kcal mole^{-1} .

(3): The practical usefulness of electrochemical generators is a function not only of energy conversion efficiency but also of the power per unit area or weight. The effect of catalysis on this position

is shown in Table III. The calculations of "maximum feasible" performances are ideal in the sense that they neglect probable increases in weight necessary to allow for heat transfer at relatively high power densities.

Thus, were adequate electro-catalysis to be attained, the increase in power density compared with that at present possible would be $>100\%$. The power per unit weight which would be attainable with adequate electro-catalysis would be that of dynamic conversion.

TABLE III

THE POSSIBLE EFFECT OF CATALYSIS ON THE POWER PER UNIT AREA AND WEIGHT OF

CERTAIN ELECTROCHEMICAL CONVERSION SYSTEMS

System	T°C	(1)			(2)		(3)	
		Watts present best	cm ⁻²	HP lb ⁻¹ present best	Watts adequate catalysis	cm ⁻² adequate catalysis	Watts maximum feasible	cm ⁻² maximum feasible
H ₂ -O ₂	67	0.154		0.023	0.250		0.250	
C ₂ H ₆ -O ₂	150	0.010		0.005	0.025		0.025	
Decane-O ₂	110	0.011		0.005	0.040		0.040	
Hg(K)-K	300	0.179		0.004	0.575		0.575	
Li-LiCl-KCl-Cl ₂	450	--		--	--		1.05	
								1.878

(1): From: Data in Table I

(2): Calculated from weight of cell, including present electrodes and solution, in (1), but with zero activation overpotential, working in solutions without marked agitation.

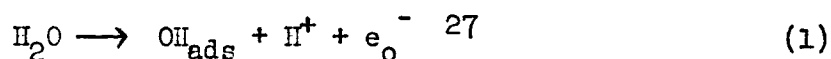
(3): Calculated by assuming that weight of system is twice times the weight of electrodes 0.002 cm thick and density 3; together with solution between them, assumed to be 0.1 cm thick; and with marked solution agitation.

II. CHEMICAL AND ELECTROCHEMICAL CATALYSIS

1. General

Any factor connected with the adsorption of the reactants and (or) products which lowers the heat of activation of the rate-determining step, increases the frequency factor or concentration of reactants, will increase the rate of reaction. In chemical catalysis, the particle which takes part in the rate-determining reaction must be: (a) sufficiently strongly adsorbed to reach finite concentration on the surface; (b) sufficiently weakly adsorbed to allow a relatively high rate constant for the rate-determining step. Thus, in the synthesis of NH_3 , N atoms must be adsorbed. Several metals adsorb N but Fe adsorbs it with heat of adsorption of only 16 kcal mole⁻¹.²⁸ On Fe substrates, the reaction with adsorbed H then becomes possible at a significant rate.

In many electrochemical reactions, the rate-determining step is a charge transfer reaction. No net charge transfer reaction is possible in a chemical reaction, and hence the important factors which are to be stressed in the electrochemical systems may differ substantially from those of the chemical ones. For example, the generalizations made above for chemical reactions would not apply to a charge transfer reaction in which, e.g.,



was the rate-determining step (see Section III.3.1).

Correspondingly, electrochemical reactions differ from chemical reactions by the fact that the surface on which they occur tends to be occupied at all conditions (at least in aqueous solutions) by a layer of oriented water dipoles. The distribution of orientations among the water molecules, however, and hence the potential difference which they contribute to the double layer p.d.,²⁹ changes with the electrode potential (Fig. 1), with possible feed back effects on the rate of charge transfer. Similarly, the surface in anodic oxidation reactions is partly occupied with adsorbed anions, and this occupancy (Fig. 2), and that of a dipolar reactant, varies with the field²⁹ in the double layer and this feeds back upon the dependence of the reaction rate on potential. Electrochemical catalysis is hence likely to be more complex than chemical catalysis, although easier to study, because the rate of the reaction, and the surface, are more easily controllable, and the species on the surface, and their concentration, can often be determined, which is seldom the case in chemical catalysis. Nevertheless, the specifically electrochemical factors mentioned are likely to be additional to those in chemical catalysis, and leading factors in this will hence be briefly mentioned.

(1) Geometric Factors

For reactions in which the rate determining step involves adsorption, or desorption of reactants or products, the lattice spacing may have influence on the velocity, or heat of adsorption.

For dissociative adsorption, the activation energy of adsorption will have a minimum, for a certain spacing, since at larger distances dissociation would have to occur before adsorption, and at smaller spacings repulsion forces retard adsorption. This aspect of catalysis has been discussed for a number of years,³⁰⁻³² and firstly by Balandin.³⁰

Heat of adsorption may be affected if adsorption involves more than one point attachment, since a molecule strained by "inadequate" distance between two sites will have a lower heat of adsorption and thus higher reactivity. Hence, lattice spacing, and the predominant crystal face on the catalyst, may have important influence. Several systems in chemical catalysis support this concept.³³

(ii) Electronic Factors

The principal electronic factors are unpaired d vacancies, and the work function. With a decreasing number of d vacancies, the heat of adsorption of the surface radicals decreases and there tends to be a corresponding increase in reaction rate. Thus, alloys are important, in particular, alloys in which a IB metal, e.g., Cu or Au, is added to a transition metal, for the IB metal adds an s electron which fills a d vacancy and the d character of the alloy can be conveniently varied. Cu-Ni and Pd-Au are systems of particular interest because during the variation of composition needed to give rise to the change in d character, little change in internuclear distance (cf. geometric factor above) occurs.

If the rate-determining step of a reaction involves desorption of an adsorbed radical, the rate should increase as the d vacancies fall until a limit is reached at which there are insufficient d vacancies for adsorption. A pioneering example in application of such an idea is Cooper and Eley's³⁴ work of 1950 in which, for the ortho-para H_2 conversion on Pd-Au, they found little change in reaction rate from 0 - 60% Au, after which the activity sharply fell. (60% of the d vacancies of the pure transition metal are unfilled).

The second electronic factor in catalysis is the work function: however, this is only so if one of the adsorbed species is ionic. If positive ions are concerned, the heat of adsorption increases with increasing work function and for negative ions, it decreases with increasing work function. Thus, Kemball³⁵, 1952, established that for the ammonia-deuterium exchange, the reactions involve the formation of NH_4^+ ions and the energy of activation decreases with increase of work function. The work function is a less important electronic factor than the d character because not many adsorbed species ionize. In electrochemical reactions,^{24,36} parallelisms of reaction rate with work function are found but the interpretation is less simple than with the gas phase reactions.

Separation of effects due to geometric factors, work function and d-band vacancies is difficult, for in few systems can one change one factor without changing the others. Thus, work functions vary with the geometric arrangement of the crystal faces of tungsten,³⁷ and with d-band character.²⁴

2. Electrochemical Catalysis

(i): Non-catalytic Factors which increase reaction rate per unit geometric area:

Apart from concentration and temperature, diffusion limitation conditions per geometric sq. cm may be improved, by e.g., porous electrode arrangements;³ or use of suspended catalyst³⁸ in intermittent contact with a collector; or by principles similar to those in which heat transfer from hot gases to liquids is maximized.

(ii): Pre-requisites for rational development of Catalysts:

Reasoning in terms of models whereby catalysis may be increased cannot be applied to a system unless at least the rate-determining step, and preferably also the path of the reaction have been firstly elucidated.

An essential characteristic of electro-catalysis is that it is potential dependent. Rate does not increase with potential in the same way for all mechanisms for a given overall reaction. Hence, catalyst A will be faster than B, for a given reaction, at an overpotential, η_1 , but the situation will be reversed at overpotential η_2 (Fig. 3). Thus, one must decide upon some potential at which the current density per true unit area is a rational measure (for comparison purposes) of the catalytic power of the given electrode. The most reasonable potential is that of zero charge,³⁹⁻⁴¹ for, here, no charge-dependent field affects the reaction rate.

Reaction rates at the potentials of zero charge on a series of electro-catalysts represents an academic and fundamental way of comparing catalytic power: it compares "the thermal part" of the electrochemical catalysis, i.e. k_0 in the equation:

$$k = k_0 e^{\frac{+}{-} (V - V_{p.z.c.})F/RT}, \quad (2)$$

where $V_{p.z.c.}$ is the potential of zero charge. Hence, knowledge and interpretation of k_0 , though important to the understanding of catalytic power, is insufficient to predict the polarization at a given potential.

It is important to note the necessity of avoiding competing reactions, when discussing the potential dependence of k . This is particularly so in oxidation reactions. An example is in Fig. 4,¹³ where the competing oxide formation on Ir and Rh shuts off ethylene oxidation at current densities too low for reasonable performance of these substrates as anodes in hydrocarbon fuel cells. The same shut off occurs on Pt at higher potentials, thus permitting the current densities to increase to a more practical value. For a given desired oxidation reaction, the thermodynamic reversible potential must be at least, say, 0.5 volts more negative than the reversible potential of the next anodic reaction possible in the system concerned.*

An important pre-requisite is knowledge of adsorption of the reactant and its dependence on potential. Knowledge of this is available

*The necessary separation depends of course upon the rate constant of the reaction, and hence upon how much polarization is necessary to attain a desirable rate.

for a few cases for H,^{42,43} (Fig. 5) and for O¹³ (Fig. 6). The adsorption of organic substances on Hg is only just becoming known.⁴⁴ The potential dependence of butyl compounds is shown in Fig. 7. Plots of the adsorption of butyl, phenyl and naphthyl compounds (under comparable potential conditions) with a number of substituents⁴⁴ are shown in Fig. 8: the variation of adsorption with structure is up to 10⁴ times.

Only a few papers concerning adsorption of organic substances on solid metals have appeared,^{45,46} or are about to be published.^{47,48} In Figures 9 and 10, adsorption of naphthalene and decylamine on Ni^{47,48} is shown as a function of potential. Substances react on electrodes only if the potential for the region in which adsorption is appreciable (region as small as 0.4 volts)⁴⁵ (Fig. 11) coincides with a potential region (for oxidation) positive to the reversible redox potential for the indicated reaction. Little discussion of this obvious point has been given, because of previous lack of data.

(iii) Factors which may increase rate constant

Understanding of such factors at present is limited to the following:

(a) Electronic factors: The comparative rates expected for a given reaction on substrates of different d character and work function can be evaluated theoretically, so long as the rate-determining step in the considered reaction is known. Suppose that the reaction concerned is the oxidation of ethylene to CO₂ and that the rate-determining reaction is the discharge of H₂O to form adsorbed OH radicals,²⁷ which then undergo a series of further reactions with adsorbed organic molecules. Then, the

standard free energy of activation for the charge transfer reaction of a water molecule to the electrode is the principal quantity which determines the rate. The major part of this is contributed to by the heat of activation for the charge transfer. If this be classical,* a potential energy profile diagram can be used to indicate the comparative effect of the work function, Φ , and adsorption energy (Fig. 12).

The State A represents the H_2O adsorbed in the double layer. It is the potential energy-distance relation for the H-O bond which is broken by the charge transfer. The curve B represents the M-OH vibration of the adsorbed radical in the final state. ΔH^{ox} is the heat of activation. Thus, this is decreased (catalysis increased) in so far as, with other factors remaining constant, the substrate is changed so as to: (a) Increase the M-OH bond strength; (b) Increase the work function.** Changes of substrate to maximize these tendencies would hence tend to maximize the catalysis, so long as such changes did not greatly change the degree of adsorption of the organic molecule undergoing (in the example chosen) oxidation. Were θ_{org} sufficiently reduced, the rate-determining step would no longer be charge transfer from H_2O but perhaps reaction of the adsorbed organic radical with OH radicals.

These remarks refer to the potential of zero charge, and in changing the substrate to attempt to follow a tendency, deduced from

*It has been so assumed in the electrochemical literature to the present time after the early suggestions to the contrary by Gurney⁴⁹ (cf. Butler,⁵⁰ but also cf. Hush⁵¹).

**But in electrochemical systems, the effect of this factor is complex, because:

considerations of the potential-energy barrier for some elucidated rate-determining step, the counter effect of change of potential from the (changed) potential of zero charge must be taken into account.

(b) Surface Configuration:. If the necessary mechanism determination has shown that (e.g., for an organic oxidation reaction) the breaking of a bond is rate-determining, the geometric factors will have effects parallel to those in chemical catalysis (see Section II,i).

Evidence exists that an increase in the defect concentration is important in increasing catalysis in some electrode reactions, e.g., the oxidation of H_2 .² Insufficient mechanism studies on anodic hydrogen dissolution exist to allow mechanistic interpretation of this fact. However, it is suggestive that if 0.1% C is introduced into zone refined Fe, the rate constant for the charge transfer to protons is increased about ten times.⁵² The local work function is less at a defect than on crystal planes. Were the charge transfer to be rate-determining and occur predominantly at points occupied by defects associated with carbon, the experimental result could be understood. One of the difficulties of study of the effect of trace inclusions in a substrate is that normally only the bulk concentration is known and Gibbs adsorption will cause the added component to be increased or decreased in the surface with respect to that in the bulk.

(c) Alloys: One basis of alloy effects has been mentioned (Section II,ii). Two others may exist: Introduction of a second component may increase the number of surface defects; and, if the less noble component (e.g., Mo in Pt) is an atom undergoing easy redox potential changes in solution, it may set up a redox system in the

double layer, which allows a change of path of the overall reaction to one having a lower heat of activation (see Section II.2.iii). None of these mechanisms has been systematically investigated. Systematic information on alloy effects is scarce except for methanol oxidation.¹⁰ Several binary and ternary alloys containing Pt, or of other noble metals exhibit higher catalytic activity than does platinized Pt (Table IV, Fig. ()). There is some evidence that to some extent the catalytic activity in methanol oxidation is paralleled in oxidation of other fuels, since Pt-Ru based catalysts exhibit improved activity for oxygenated and paraffinic hydrocarbons. The enhanced catalysis alloys in methanol oxidation cannot be explained by physical properties such as surface area, since this is, e.g., about the same for the active Pt-Ru alloys (Table IV) as for Pt black. However it is difficult to relate the catalysis to merely electronic factors, since a number of ternary alloys with widely varying electronic characteristics perform equally well in binary compositions. Activation energies for oxidation on Pt and Pt-Ru alloys are also similar.

It is thus probable that increase in the concentrations of surface defects on the alloyed catalyst, compared with the pure metal, gives the origin of the catalysis.

(d) Semiconductor surfaces: Electrode kinetics on semiconductors has been formulated fairly recently,⁵³⁻⁵⁷ and the use of boride⁵⁸ and carbide electrodes⁵⁹ in oxidation reactions was first reported in 1963. Ni_2B proved to be a good catalyst in hydrazine oxidation⁶⁰ (0.1 V less polarization than Pd). As an anode in H_2 oxidation at 80°C it showed only 40 mV higher polarization than a Pd/graphite anode in the range from 65 to 260 mA cm^{-2} .⁵⁸

TABLE IV¹⁰COMPARISON OF THE CATALYTIC ACTIVITY OF Pt BLACK AND NOBLEMETAL ALLOYS IN METHANOL OXIDATION

Metal or alloy	Polarization in 2N H ₂ SO ₄ at 100°C at 20 mA cm ⁻² (V)	Remarks
<u>Pt black</u>	0.44	
<u>Binary alloys of Pt with base metals</u>		
of Group IVB and VB VIB and VIIB	0.37-0.39 0.20-0.38	Best: Pt67 Mo33 - 0.20 Pt80 Re20 - 0.29 Pt67 Re33 - 0.31
Fe, Ni, Co, Be, Pb, Cn, Bi, Sb	Similar, or decreased activity as compared with Pt black	
<u>noble metals</u>		
Ru	0.24-0.32	Optima for 20% Ru - (Pt Ru) 33% Ru - (Ru ₂ Pt)
Os	0.30-0.35	
Rh	As Pt black	
Ir (25%)	0.33	
<u>Binary Pt free alloys</u>		
Ru - Rh	0.29-0.38	Optimum for Ru 90 Rh 10
Ru with Pd, Ir, Rh Os, with Pd, Ir, Rh	0.38-0.46	
<u>Ternary alloys of Pt + Ru with</u>		
W	0.25-0.37	
Ta	0.24-0.27	
Zr	0.30	
Mo	0.23	(Pt 70 Ru 15 Mo 15)

The catalytic activity of Ni_2B seems to be connected primarily with the chemisorptive properties. The coverage with hydrogen varies from 0.1 to 0.0 depending on the thermal pretreatment of the electrode, whilst the reaction rate decreases about 10^6 times.

Control of the electron energy levels in a semiconductor by the choice of suitable donor and acceptor species makes possible a particular well-controlled model system for work in electro-catalysis.

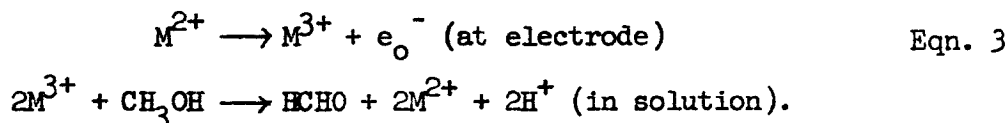
(e) Imposed pulses of potential: Suitable pulses (say, an anodic pulse to cover the electrode with O and a cathodic pulse to remove this layer, with a pulse time of 10^{-3} sec.) should clean the surface from inhibiting impurity layers which may build up there, and hence maintain catalysts of constant activity. The possibility that grain growth can also be controlled exists because the size of grains which nucleate is potential dependent. Whether the imposing of repeated pulses can bring about increase in catalysis, apart from removal of impurities, is not established. In principle, the momentary dissolution of surface atoms, i.e., the creation of defects, should be attainable.

An example from unpublished work is given in Fig. 13, which shows the increase by several orders of magnitude of the rate of oxidation in the diagram. Pulsing may be effected by short circuiting the cell for 0.1 sec intervals every few seconds.

(iv) Use of Redox Systems to change the path of the overall reaction:

Considering, for example, the oxidation of methanol to CO_2 , and that the rate-determining step in this reaction is charge transfer

from CH_3OH to the substrate, catalytic effects should be observed if a redox couple is present which has (a) a standard potential in the neighborhood of the reversible potential; * (b) i_0 values for charge transfer much greater than those exhibited by the direct charge transfer from the organic; (c) a sufficiently high rate constant for the subsequent homogeneous phase oxidation. Then:



etc.

This principle can be successfully applied (with the nitrous-nitric couple, having an e_0 of 0.94)⁶¹ in overcoming the difficulties⁶² associated with making practical reversible oxygen electrodes, where the i_0 involved in the oxygen dissolution reaction is of the order of 10^{-10} amps cm^{-2} . A similar principle might be used to reduce the overpotential which needs to be applied to hydrogen-oxygen generators, e.g., the manganous-manganic couple, which has a standard redox potential in acid solution of 1.5 volts.⁶¹

(v) Photo, sono, radioactive and radio-galvanic effects:

The basic theory of photo⁶² and sono effects^{63,64} has been known for some time. Large photo-effects (decreases of overvoltage by 0.5 volts) have been observed upon c.v. irradiation of Si.⁶⁵ Very significant acceleration of the oxygen reduction reaction by α emitters dissolved in the substrate has been established, but the interpretation

*The reversible potential of the redox couple cannot be greatly (i.e., > 0.1 volt) changed by adjustment of the redox ratios because of the necessity of maintaining satisfactory limiting current conditions.

is unclear.^{66,67}

III. THE MECHANISM OF SOME ELECTROCHEMICAL REACTIONS OF INTEREST IN DIRECT ENERGY CONVERSION

The necessity of knowing the mechanism of the reaction as a pre-requisite to rational variation of the catalyst in a favorable direction makes it appropriate to discuss briefly some mechanisms of relevant reactions.

1. The Anodic Hydrogen Dissolution Reaction (h.d.r.)

The cathodic evolution of hydrogen is a much studied electrode reaction. The relative simplicity which might be expected for this reaction has not enabled a completely clear solution of the mechanism to be obtained, because of the following difficulties:

(i) The alternatives of a rate-determining proton discharge and a combination of a proton with an adsorbed H with accompanying neutralization have theoretically predicted characteristics which are very similar. Distinction between these alternative steps is in practice difficult to make, unless it is possible to measure the amount of adsorbed H on the surface of the electrode as a function of the reaction rate,^{15,16} a difficult determination in acid solutions on non-noble metals.⁴³

(ii) A distinction between these alternatives could be obtained on the basis of separation factors,¹⁶ so long as the degree of proton tunnelling⁶⁸ is known. However, this aspect of affairs is not yet established,⁶⁸ and the certainty of the separation factor method depends on this.

Few mechanistic studies of the mechanism of the hydrogen dissolution reaction¹⁷ have been made. The most probable position concerning the evolution reaction is summarized in Table V.

TABLE V
PROBABLE MECHANISMS OF THE CATHODIC HYDROGEN EVOLUTION REACTION

Metal	pH (approx)	Path	Rate deter- mining step	Main lines of evidence
Hg, Pb	0.3	Coupled discharge electrochemical	Discharge	Tafel slope ΔH vs $\log i_0$ $\theta(\text{Hg})^{52}$ separation factor ⁴
Cu, Ni	0.3	Discharge Electrochemical	Electrochemical	Tafel slope ΔH vs $\log i_0$ separation factor
W	0.3	Coupled discharge Electrochemical	Electrochemical	Tafel slope ΔH vs $\log i_0$ separation factor
Pt, Rh	0.3	Discharge recombination	Recombination	Tafel slope separation factor
Ni, W	13.7	Discharge recombination	Discharge	Tafel slope stoichiometric No (Ni) $\log i$ vs \log θ (Ni) separation factor
Pb	13.7	Coupled discharge electrochemical	Discharge	Tafel slope ΔH vs $\log i_0$ Separation factor
Pt	13.7	Discharge electrochemical	Electrochemical	Tafel slope separation factor

To what extent do the probable mechanisms of the hydrogen evolution reaction of Table V apply to the dissolution reaction important in electrochemical energy conversion? As argued elsewhere,⁶² the mechanism of the cathodic and anodic reactions must be the same at the reversible potential: further, if the Tafel cathodic and anodic

lines extrapolate to the same i_0 at the thermodynamically reversible potential, then the mechanism of the anodic reaction must be the same, for the potential range of that line, as that for the cathodic reactions. Unfortunately, this has usually been assumed in discussing the mechanism of the anodic reaction. Insufficient data exist to justify the assumption.

A limitation on the applicability of the present experimental data on the kinetics of the reactions of hydrogen to electrochemical energy conversion concerns the fact that the fundamental mechanism work on evolution has been done on massive (plate or wire) electrodes, whereas in electrochemical generation the electrode material is often on finely divided particles of material, isolated from each other, on a relatively inactive substrate (Pt on porous C), or of a special construction (e.g., Ni in which defects have been introduced by dissolution of Al for Ni-Al alloys). To extrapolate knowledge from the solid substrate mechanisms is dangerous.

2. Oxygen dissolution (and evolution) reaction

It is not intended here to discuss this reaction in any detail, for it is fully treated elsewhere in this Symposium. In the following, only the essential problems in this central problem in fuel cell kinetics will be mentioned.

Studies of the mechanism of oxygen dissolution and evolution are subject to the following difficulties:

(i): The range of metals upon which evolution can be observed in any simplicity is limited to the noble metals and their alloys, because of build up of oxide films on other materials.

(ii): Reactions involving H_2O_2 may occur which complicate the situation, particularly the mechanism of the potential observed on open circuit. These are:



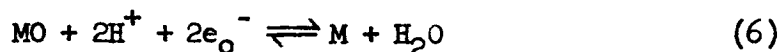
A substantial measure of agreement exists concerning the mechanism of (4), which is suggestive in discussing (3). The essential point is that the path does not involve an intermediate of adsorbed O .⁷⁰⁻⁷³ Charge transfer occurs directly to O_2 .

This mechanism suggests⁷⁴ that reaction (3) may be regarded as the sum of (4) and (5), with the important corollary that adsorbed O would not be important. A critical experiment bearing on this (and analogous to the critical experiment of Davies, Clark, Yeager and Hovorka⁷³) was carried out by Rosenthal and Veselovski,⁷⁵ who examined O_2 evolved from a surface containing O^{18} . The evolved gas did indeed contain O^{18} , in contradiction to the suggestion indicated above, but the possibility of exchange with the solution was not investigated. Tafel parameters of the evolution reaction are not consistent with the reaction $\text{O}_2^- \rightarrow \text{O}_2 + \text{e}_\text{o}^-$ as the rate-determining step.

An important question concerns the zero current potential for an inert electrode immersed in a solution containing O_2 . Under practical conditions, this is not the thermodynamically reversible potential but a potential of 0.9 - 1.0 volt.* This "loss in potential" clearly has

*Observation of the reversible potential is possible.

significance for fuel cell reactions. One would attempt to interpret it predominantly in terms of a mixed potential between at least one cathodic and one anodic reaction of the above set of reactions. Quantitative consideration is successful in bringing consistence into the data except the vital one of the origin of the necessary H_2O_2 . Thus, this must arise from some unsuspected reaction occurring at a potential negative to 1.23. Also, there may be a part played by oxide equilibria of the type^{76,77}



A third, and radical, suggestion is that, in the time in which observations are usually carried out, there is no time for charge transfer equilibria to occur (come to steady state) so that the interface must be regarded as polarizable and the problem treated like one in adsorption and not in kinetics.⁷⁸

Certain critical experiments are urgently necessary in the study of this reaction:

(a): O^{18} exchange experiment in which ambiguity of exchange with solution by measuring this firstly will be eliminated.

(b): O^{18} experiments should be used to obtain the kinetics of electrochemical equilibration of oxides.

(c): The existence, or not, of important potential-determining effects from oxide equilibria can be established by a pH variation experiment with extreme deoxidation of the solution. A simple RT/F relation is expected.

3. The Anodic Oxidation of Hydrocarbons

The oxidation of hydrocarbon at low temperatures has acquired

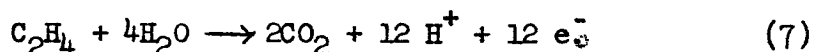
recently a great interest. However, the literature⁷⁹⁻⁸¹ concerns predominantly technological aspects.

Investigation of the reaction mechanism was started at the University of Pennsylvania about three years ago.^{6,27,32-34} The mechanism of oxidation of several olefins (ethylene,²⁷ propylene, allene, 1-butene, 2-butene³⁴) and of acetylene⁶ has been studied on platinum at 80°C.

Apart from small differences in i_0 and coulombic efficiency, the electrochemical behavior and main reaction products were similar for all olefins (Table VIII) and the mechanism of their oxidation will be discussed in the example of ethylene.

i. Oxidation of ethylene (as representative of olefins)

The overall reaction yields CO_2 with $100 \pm 1\%$ coulombic efficiency in acid and $90 \pm 5\%$ efficiency in alkaline solution. Thus, branching reactions leading to products other than CO_2 and water (or protons) are neglected* and the half-cell reaction can be written as:



The observed Tafel slopes for the pH range 0.3 - 12.5 and pressure range from 10^{-3} to 1 atm are $b = 140 - 160$ mV (Fig. 14). At 80°C, the theoretical value of $b = 2.3 \times \text{RT}/\alpha\text{F}$ for $\alpha = 0.5$ is 140. Thus, a charge transfer is a rate-determining step and the value of α is between 0.44 - 0.5.

*However, a branching reaction of a current efficiency below that which can be detected in acid solutions could occur and inhibit catalysis increasingly with increasing time (see below).

TABLE VIII

DIAGNOSTIC CRITERIA FOR OXIDATION OF HYDROCARBONS ON Pt AT 80°C IN 1 N H₂SO₄

Hydrocarbon	Tafel Slope	% Coulombic Efficiency for complete oxidation	Exchange Current Density (A cm ⁻²)	($\frac{di}{dp}$) _{V, pH}	($\frac{d \log i}{d \log c_{H^+}}$) _V	($\frac{dV}{d \log c_{H^+}}$) (mV)	($\frac{d\eta}{d \log c_{H^+}}$) (mV)	($\frac{d \log i_o}{d \log c_{H^+}}$)
Ethylene	$\frac{4.6RT}{F}$	100	4×10^{-8}	< 0	-0.45	65	0 - 10	~ 0
Allene	$\frac{4.6RT}{F}$	93	2.9×10^{-8}	< 0	-0.41	68	0 - 10	~ 0
Propylene	$\frac{4.6RT}{F}$	97	2.5×10^{-8}	< 0	-0.35	52	0 - 20	~ 0
1-Butene	$\frac{4.6RT}{F}$	71	1.8×10^{-8}	< 0	-0.47	67	0 - 10	~ 0
2-Butene	$\frac{4.6RT}{F}$	83	1.8×10^{-8}	< 0	-0.45	66	0 - 10	~ 0
Acetylene	$\frac{2.3RT}{F}$	100	10^{-18}	< 0	-0.8	~ 50	0 - 20	~ 0

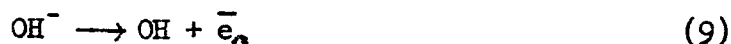
The observed Tafel slope is consistent only with the first charge transfer, or a later charge transfer from the species present at the electrode at full coverage, as the step which determines the rate of the overall reaction. In the latter case, no pressure effect could be expected.

This however exists (Fig. 15) in the sense that the steady state reaction velocity decreases with increase of pressure. Thus the value of $b = 2.3 \text{ } 2RT/F$ together with the fact that $di/dp < 0$ fix the location of r.d.s. as the first charge transfer reaction.

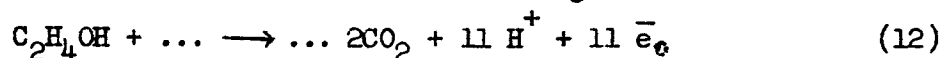
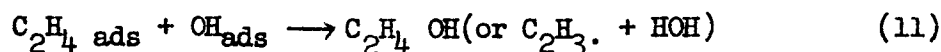
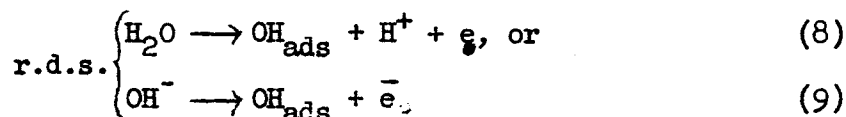
(The inverse pressure effect could be caused by a build up of a side product, possibly a polymer, of the reaction. The evidence on this hypothesis is not yet conclusive, but its balance appears to be negative. Thus, the pressure effects are reversible on repeated pressure changes without hysteresis. Similar effects have been observed on Pt with other hydrocarbons, but not during ethylene oxidation on some other noble metals where positive pressure effects occur, with a radically different dependence of current density upon potential, i.e. a different mechanism^{*}).

The negative pressure effect: $di/dp < 0$ shows that r.d.s. involves a substance which requires the surface free of ethylene (or any intermediate derived therefrom) to adsorb. Thus the likely rate-determining step is one of the two reactions:

^{*}However, it is noteworthy that the mechanism discussed here does depend in an important way upon the conclusions that the pressure effects arise directly as a result of the mechanism and not as a consequence of secondary inhibition. It is desirable to obtain further evidence on this point.

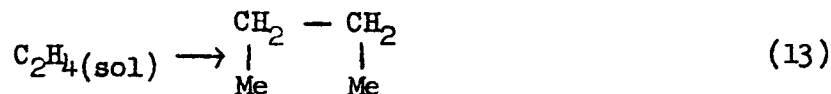


The reaction sequence may then be represented by



This deduction can be shown to be consistent with the negative pressure effect in the following way. According to the hypothesis, the coverage of all intermediates will be negligible in comparison with the coverage by the ethylenic radical, since they occur after the rate-determining step and are not in equilibrium because of the constant removal of the final product, CO_2 . Thus it is justified to assume that $\theta_{\text{Total}} \sim \theta_{\text{ethylene}}$.

The model for ethylene adsorption under anodic conditions deduced on the basis of considerations of the energy of adsorption, is



Thus, the adsorption of ethylene molecules involves four surface sites of Pt per one molecule of ethylene. The adsorption isotherm is then of the form

$$\frac{\theta}{(1 - \theta)^4} = K_p P_E \quad (14)$$

where $\theta = \frac{\int}{\int_{\text{max}}}$ fractional coverage with ethylene, K_p - equilibrium constant (atm^{-1}), P_E - partial pressure of C_2H_4 . On the basis of

independent radio-active measurements,⁸⁵ the coverage of Pt with organic θ_E was estimated to be relatively potential invariant in the potential range of Tafel region, and equal to ~ 0.7 . For this value of θ at $P_E = 1$ atm, $K_p \approx 150 \text{ atm}^{-1}$.

Now, for the postulated mechanism, the current is given by:

$$i = k_2 a_{H_2O} (1 - \theta_E) e^{\alpha FV/RT}, \text{ or} \quad (15)$$

$$i = k'_2 a_{OH^-} (1 - \theta_E) e^{\alpha FV/RT}, \quad (16)$$

and at constant potential, the current decreases with pressure as the term $(1 - \theta_E)$ does.

From the theoretical plots of $(1 - \theta)$ versus P_E , for $K_p = 150 \text{ atm}^{-1}$, the values of $(1 - \theta)$ at $P_E = 1, 0.1, 0.01$ and 0.001 atm were found and introduced into equation (15). The term $k_2 a_{H_2O} e^{\alpha FV/RT}$ was calibrated from the experimental value of i at $P_E = 1$ atm and 520 mV and the theoretical $i - \log p$ relationship for seven potential values was plotted and is shown in Fig. 16, 16a. The points correspond to the experimental data, and are in fairly good agreement with the theory.

Further support for the hypothesized mechanism is as follows.

Independently of the number of carbon atoms, of number of double bonds, and of their position in the olefins studied, the kinetic parameters remain the same, and the exchange current changes by less than a factor of 2 (Table VIII). This is strong support, for, were the rate-determining charge transfer to include an organic radical, i_0 should change significantly with structure.

Whether H_2O or OH^- takes part in the rate-determining charge

transfer can be discussed in terms of the $\log i$ - pH relationship (Fig. 17). The value of $(d \log i / d \text{pH})_v$ is constant over the whole pH range, suggesting that the same mechanism applies in the cases of both acidic and alkaline solutions. Charge transfer from OH^- ions would cause, in acid solutions, a limiting current at low current densities. Discharge occurs from water molecules.

The present model is not consistent with the theoretical coefficients (derived on a simple model) for water or OH^- ions discharge as the rate-controlling step (Table IX). This fact does not militate

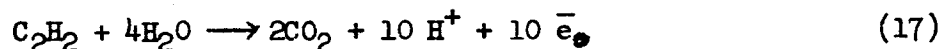
TABLE IX
EXPERIMENTAL AND THEORETICAL pH DEPENDENCE IN CERTAIN REACTIONS
INVOLVING THE DISCHARGE OF H_2O OR OH^- IN PRESENCE
OF EXCESS NEUTRAL SALT

Origin	$(\frac{d \log i}{d \text{pH}})_v$	$(\frac{d \log i}{d \text{pH}})_i$	$(\frac{d \log i_o}{d \text{pH}})$
Theoretical consideration (Discharge from water of the simple model)	0	RT/F	$-\alpha$
(Discharge from OH^-)	1	$-RT/F$	α
Bockris & Huggins ⁸⁶ , O_2 evolution on Pt, (H_2SO_4)	0.25	$\alpha RT/F$	
Vetter & Berndt ⁸⁷ , O_2 evolution on Pt wide pH range		0	
MacDonald & Conway ²⁵ , O_2 evolution on Pd and Au alloys (H_2SO_4 , NaOH)		0	0
Wroblowa, Piersma, & Bockris ²⁷	0.45	~ 0	~ 0

against the suggested mechanism but lends it support because similar anomalous pH effects were observed by authors^{25,86,87} (Table IX) who were concerned with simple reactions in which the probability of rate-determining charge transfer from H_2O is very high.

ii. Mechanism of acetylene oxidation⁶

The efficiency of CO_2 production is $100 \pm 1\%$ in acid and $95 \pm 5\%$ in alkaline solution for a reaction



The Tafel slope is here $\sim 70 \text{ mV} = 2.3RT/F$ (Fig. 18) and $di/dp < 0$.

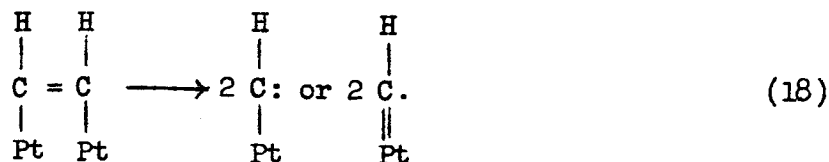
Similar reasoning as above leads to the conclusion that the observed Tafel slope of $2.3RT/F$, together with the existence of the pressure effect, must be associated under Langmuir conditions with a chemical reaction following the first charge transfer.

The negative pressure effect observed ($di/dp < 0$) shows that the r.d.s. must include a substance other than the adsorbing acetylene or a radical derived from acetylene. Since all kinetic parameters are the same in acidic and alkaline solutions, including the pH effect (Fig. 19), the same mechanism may be assumed for both. This points to the OH radical being the entity in question. This in turn (in acidic solutions) may arise only from water discharge. Thus the charge transfer preceding the r.d.s. is water discharge:



The rate-determining chemical reaction involves, apart from OH, either adsorbed acetylene, or a radical derived therefrom, in a chemical reaction. (Any dissociation into H atoms would involve ionization into $\text{H}^+ + \text{e}^-$ and contribute to the Tafel slope.) Hence, the radical derived from acetylene can be only CH or an addition product involving acetylene and water.

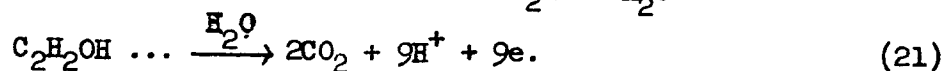
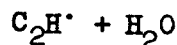
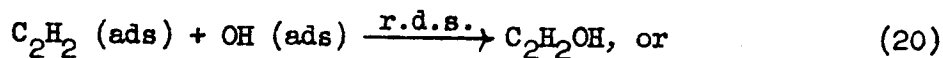
The adsorption of acetylene followed by splitting, i.e.,



would require additional energy connected with breaking of the double bond of about $146 \text{ kcal mol}^{-1}$. Even if each carbon atom were to form not one, but two covalent bonds with Pt, the extra energy needed would be about 80 kcal mol^{-1} . Therefore, the possibility of CH being the radical seems unlikely.

It is difficult to distinguish whether the radical in question is adsorbed acetylene or a product of water addition since both would give similar kinetic parameters. Absence of polymerization products and of acetaldehyde in the electrolyte indicate there is no hydrolysis in solution. It is therefore likely that the radical is assumed to be adsorbed acetylene.

The reaction path may be now formulated along the lines of:



From the quasi-equilibrium in reaction (8),

$$\theta_{\text{OH}} = K_5 (1 - \theta_{\text{T}}) a_{\text{H}^+}^{-1} e^{FV/RT} \quad (22)$$

The coverage of OH radicals in the potential range is low¹³ and the coverage of all other intermediates may be neglected in comparison

with θ_A , since they occur in the reaction sequence after the rate-determining step, and are not in equilibrium because of the constant removal of the final product, CO_2 . Thus the total coverage θ_T may be approximated as $\theta_T \simeq \theta_A$.

The rate of anodic oxidation of acetylene may then be expressed as

$$i = nFK_5 k_6 a_{\text{H}^+}^{-1} \theta_A (1 - \theta_A) e^{FV/RT} \quad (23)$$

For $\theta_A > 0.5$ a negative pressure effect will be observed. A rough estimate of θ_A and K_{P_A} was made on the basis of the comparison of solubilities and energies of adsorption of both gases,³² leading to the conclusion that $\theta_A > \theta_E$. Comparison of theoretical and experimental kinetic parameters is shown in Table X.

TABLE X
Kinetic Parameter for Acetylene Oxidation

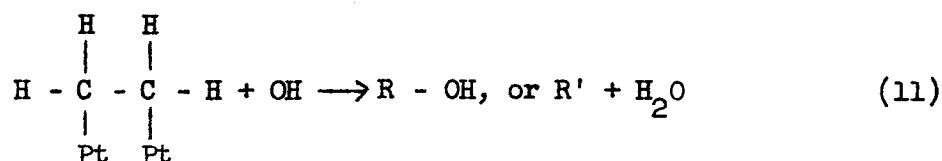
Kinetic parameter	Theoretical value	Experimental value
At constant ionic strength		
Tafel slope	$2.3 \text{ RT/F} = 70 \text{ mV}$	$65 \sim 75 \text{ mV}$
pH dependence, assuming $\theta_A \neq f(\text{pH})$	$(\frac{\partial \log i}{\partial \text{pH}})_V = 1$	0.8
	$(\frac{\partial V}{\partial \text{pH}})_i = -70 \text{ mV}$	$\sim 50 \text{ mV}$
	$(\frac{\partial \log i_0}{\partial \text{pH}}) = 0$	~ 0 (cf. Section 3.1)

The consistence of the postulated mechanism with experiment also exists in respect to the pressure effect. This was calculated in an analogous manner as that described for C_2H_4 oxidation and the agreement between theoretical and experimental values, shown in Figure 20, seems satisfactory.

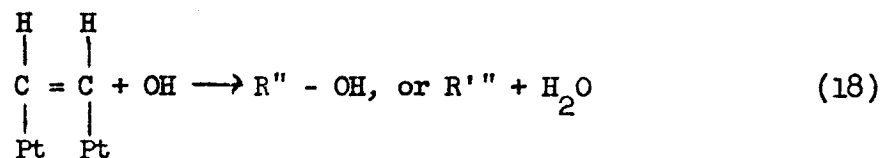
iii. Effect of the triple bond

The mechanisms proposed for olefin oxidation involves a rate-determining water discharge reaction, whereas that for acetylene involves a rate-determining reaction between adsorbed acetylene and OH radicals. That the systems have a difference in mechanisms arises probably from a higher value of the heat of adsorption of acetylene as compared to that of ethylene as a result of the triple bond in the former.

For the case of ethylene, the specific rate of the reaction



is higher than that of water discharge, whereas for acetylene, the specific rate of the reaction



is less than that of water discharge. This results in a change of the Tafel slope from $2RT/F$ to RT/F and a greatly reduced i_0 value.

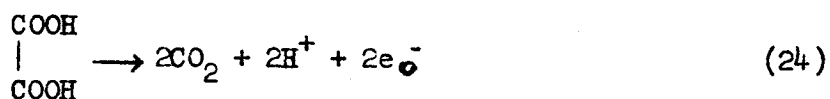
iv. Effect of the oxide formation

In the oxidation on Pt of paraffins,⁸⁸ olefins,^{27,84} as well as of

acetylene,⁶ under potentiostatic conditions, current drops to negligible values at $V \approx 0.9 - 0.95$ V (against hydrogen electrode in the same solution) and does not increase until the potential of O_2 evolution is reached. On the other noble metals, this "passivation" occurs at different potentials (cf. Section IV.3, Fig. 21), which always coincide with the potential at which ~ 0.2 of the electrode surface is covered with oxygen. The observed passivation with respect to ethylene oxidation may be understood if at potentials above $V \approx 0.9$ V the reaction between OH radicals, or OH and H_2O occurs fast enough for the accumulation of PtO (or $Pt(OH)_2$) and water discharge onto the PtO covered surface drops to a negligible rate.

4. Anodic oxidation of oxalic acid⁸⁹

Oxalic acid is also completely oxidized to CO_2 in acidic solution according to the reaction:

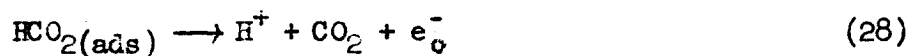
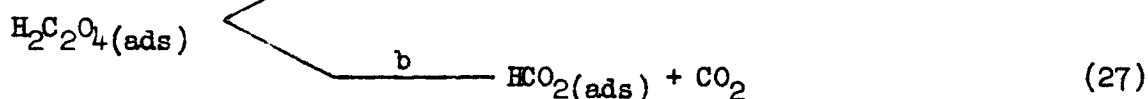
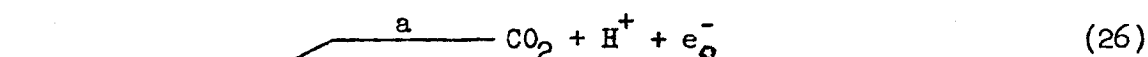
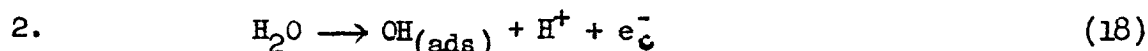
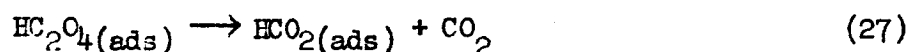
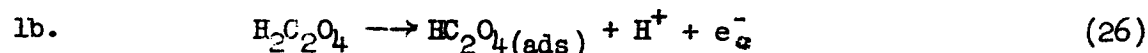
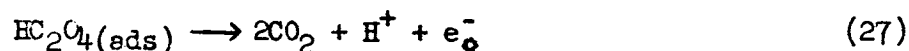
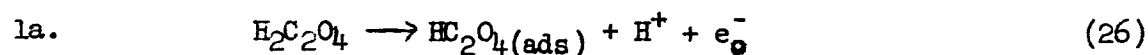


No reaction was observed in alkaline medium. This fact together with the analysis of the reaction order with respect to unionized acid and a hypothetical univalent acid anion led to the conclusion that the reacting species is a unionized molecule. For this, relatively simple, reaction either (i) both electrons may originate with the organic substance; or (ii) one electron may be transferred from the organic, another in the production of an oxidizing agent, e.g., $H_2O \longrightarrow OH + H^+ + e^-$; (8) both electrons may be transferred in the production of an oxidizing agent.

The empirical kinetic equation obtained is

$$i = k c_{\text{H}_2\text{C}_2\text{O}_4}^{0.35} c_{\text{H}^+}^{-0.55} e^{FV/RT} \quad (25)$$

Several (~ 25) schemes which may represent the reaction sequence in the oxalic acid oxidation have been analyzed and kinetic equations and parameters derived both under Langmuir and Temkin conditions. The latter conditions were examined for the first time with respect to the reaction orders. Reasonable consistence of the experimental kinetic parameters can be obtained only with the following schemes under Temkin conditions:



Assuming that:

(i) The total coverage of the electrode is in the intermediate range ($0.2 < \theta_T < 0.8$).

$$(ii) \quad \Delta G_{\theta}^0 = \Delta G_{\theta=0}^0 - f(\theta) = \Delta G_{\theta=0}^0 - \sum r_i \theta_i \quad (30)$$

where $r_i = - \partial (\Delta G_{\theta_i}^0) / \partial \theta_i$.

The kinetic equations for the above schemes are as follows:

$$1a. \quad v_3 = k_3 c_{\text{ox}} (1 - \theta) e^{\alpha FV/RT} e^{-\{\Delta G_3^\ddagger + \beta f(\theta)\}/RT} \quad (31)$$

$$v_{-3} = k_{-3} c_{\text{H}^+} \theta e^{-(1-\alpha)FV/RT} e^{-\{\Delta G_3^\ddagger - (1-\beta)f(\theta)\}/RT} \quad (32)$$

where ΔG^\ddagger = standard free energy of the activated complex, β is the symmetry factor, $k_i e^{-\Delta G_i^\ddagger/RT}$ is the specific rate constant for the i th step in the reaction sequence, V is the Galvani potential and c_i is concentration in the double layer (assumed equal to that in the bulk, because of the high and constant ionic strength of the solution).

For quasi-equilibrium, $v_3 = v_{-3}$; neglecting the changes in the $\frac{\theta}{1-\theta}$ term as compared with the exponential term in θ , and assuming $\beta = 0.5$

$$f(\theta) = FV + RT \log c_{\text{ox}} - RT \log c_{\text{H}^+} + \text{const} \quad (33)$$

$$v_4 = k_4 \theta e^{\alpha FV/RT} e^{-\{\Delta G_6^\ddagger - \gamma f(\theta)\}/RT} \quad (34)$$

assuming $\gamma \sim 0.5$,* neglecting the pre-exponential term in θ , and introducing $f(\theta)$ from Eq. (33),

$$v_4 = k_4' e^{FV/RT} c_{\text{ox}}^{0.5} c_{\text{H}^+}^{-0.5} \quad (35)$$

1b If reaction (28) is the r.d.s.

$$v_6 = k_5 \theta_{\text{HCO}_2} e^{\alpha FV/RT} e^{-\{\Delta G_6^\ddagger - \gamma f(\theta)\}/RT} \quad (36)$$

From equilibrium in eq. 26:

$$f(\theta) = FV + RT \log c_{\text{ox}} - RT \log c_{\text{H}^+} - RT \log \left(\frac{\theta_{\text{HCO}_2} \theta_4}{1 - \theta_T} \right) + \text{const} \quad (37)$$

The logarithmic term in θ may be neglected independently of the

*Symmetry factors are defined in the further analysis as γ , and are assumed to be always close to 0.5.

value of $\theta_{\text{HC}_2\text{O}_4}$ as compared with θ_T , since from equilibrium in (27) assuming c_{CO_2} to be constant,

$$\theta_{\text{HCO}_2} = K'_3 \theta_{\text{HC}_2\text{O}_4} \quad (38)$$

and

$$\theta_{\text{HC}_2\text{O}_4} = \theta_T \left(\frac{1}{1 + K'_3} \right) \quad (39)$$

Hence $f(\theta)$ is again expressed as in Eq. (34).

By similar argument θ_{HCO_2} may be neglected in Eq. (36) (as compared with the exponential term in θ), since $\theta_{\text{HCO}_2} = \frac{K'_5 \theta_T}{1 + K'_5}$.
Hence

$$v_6 = k_6 e^{FV/RT} c_{\text{ox}}^{0.5} c_{\text{H}^+}^{-0.5} \quad (40)$$

2a. If reaction (26) is the r.d.s.

$$v_4 = k'_4 \theta_{\text{HC}_2\text{O}_4} e^{\alpha FV/RT} e^{\gamma f(\theta)/RT} \quad (41)$$

Since $\theta_{\text{HC}_2\text{O}_4} \approx \theta_T$, from quasi-equilibrium in (8):

$$\theta_{\text{OH}} = k'_7 e^{FV/RT} c_{\text{H}^+}^{-1} e^{-f(\theta)/RT} (1 - \theta_{\text{HC}_2\text{O}_4}) \quad (42)$$

From quasi equilibrium in (30):

$$\theta_{\text{HC}_2\text{O}_4} = K'_8 c_{\text{ox}} \theta_{\text{OH}} \quad (43)$$

Introducing θ_{OH} from (42) into (43), and neglecting the pre-exponential terms in coverage,

$$f(\theta) = FV + RT \log c_{\text{ox}} - RT \log c_{\text{H}^+} + \text{const.} \quad (44)$$

Introducing $f(\theta)$ into equation (41) and neglecting the pre-exponential term in θ

$$v_4 = k'_4 e^{FV/RT} c_{\text{ox}}^{0.5} c_{\text{H}^+}^{-0.5} \quad (45)$$

2b. If reaction (28) is the r.d.s.,

$$v_6 = k'_6 \theta_{\text{HCO}_2} e^{\alpha FV/RT} e^{\gamma f(\theta)/RT} \quad (46)$$

$f(\theta)$ is again expressed by Eq. (33) and by the same argument as in 1b

$$v_6 = k_6' e^{FV/RT} c_{\text{ox}}^{0.5} c_{\text{H}^+}^{-0.5} \quad (47)$$

Further distinction between these schemes cannot be made directly on the basis of the electrochemical evidence available. However, the results obtained in the oxidation of hydrocarbons indicate that the rate of a reaction sequence involving water discharge (reaction 8) as the r.d.s.,²⁷ or in quasi-equilibrium,⁶ drops almost to zero at potential region above $\sim 0.9\text{v}$. Since no passivation of this type was observed in the oxidation of oxalic acid, it may be inferred, that the most probable reaction sequence is scheme 1, in which both electrons are supplied by the organic species. Further distinction between 1a and 1b is not yet possible.

IV: THE MECHANISM OF ELECTRO-CATALYSIS

1. Hydrogen

A crude interpretation of the trends in acid solutions was suggested by Conway and Bockris in 1957.²⁴ This was based upon plots of η (c.d. 10^{-3} amp cm^{-2}) against the value (for most metals calculated), of the metal-hydrogen bond strength (see Fig. 22). One clear group is discernable (the transition metals) and a second group (Hg, Pb, Tl) exists with a weak indication of the direction of the dependence of η upon D_{MH} . The latter group of metals do, in any case, have i_0 's which are very different, in orders of magnitude, from those which the transition metals have at comparable D_{MH} values. The few points on these low i_0 metals are at least not inconsistent with the view that, for them, i_0 becomes larger as the MH bond strength increases. Conversely,

for the transition metals, i_0 decreases as D_{MH} increases. Correspondingly (Fig. 23), for the transition metals a relation between the exchange current density values and the number of d vacancies exists, in the sense that i_0 decreases as the number of d vacancies increases.

These correlations would seem to favor the proton discharge reaction as rate-determining on Hg, Pb and Tl and the desorption reaction with charge transfer rate-determining for the transition metals. Thus (see Fig. 24), if the potential energy of the final state is proton discharge is lowered (higher bond strength), the rate at a given potential will increase; but for electrochemical desorption as a rate-determining step, it will be (Fig. 25) more difficult to carry out the reaction as the MH bond strength increases.⁹⁰

The noble metals form a third group in Conway and Bockris,²⁴ discussion: under conditions in which their i_0 's are sufficiently high, the h.e.r. is determined by the atomic combination reaction.^{91,92} Controversy exists concerning the mechanism of hydrogen evolution on the noble metals. Thus, Breiter,¹⁷ supported by Frumkin,⁹³ regards the rate-determining step as the diffusion of molecular H_2 in solution away from the electrode. It is clear that at a sufficiently high i_0 for the charge transfer and desorptive reactions, a diffusion step must become rate-determining. The question is, how high must the i_0 for the hydrogen evolution reaction on noble metals be for the overall reaction to be no longer controlled by the chemical combination step. In the region of current density when bubbles form, rate control by diffusion of H_2 away from the surface appears not to be an acceptable rate-determining mechanism. Bubbles usually form in hydrogen evolution at current

densities of about 10^{-3} amp cm^{-2} .

Several criticisms may be made of the Conway and Bockris analysis.

Thus:

(i) The rates are compared at the reversible potentials, whereas they should be compared at the potential of zero charge,³⁹⁻⁴¹ (although some of these are not available).

(ii) The values the H bond strength with which the rates of the h.e.r. at the reversible potentials are compared (those from the gas phase at zero coverage) are not necessarily the valid ones. The bond strength decreases with increase of surface coverage in a gas phase reaction. For the rate-determining $\text{H}^+ + \text{e}_\text{o}^- \longrightarrow \text{H}_\text{ads}$, the θ values are expected to be relatively low,^{14,42,94} and hence the values used are probably valid for purposes of comparison. But, for the $\text{H}^+ + \text{H}_\text{ads} + \text{e}_\text{o}^- \longrightarrow \text{H}_2$ reaction, the surface coverage in the steady state is probably high,⁴² and the values would be lowered compared with those used in the plot in Fig. 22.

The last criticism may perhaps be met when it is recalled that the coverage is likely to be of the same order (> 0.9) on all metals, for the h.e.r. under conditions of rate-determining $\text{H}^+ + \text{H}_\text{ads} + \text{e}_\text{o}^- \longrightarrow \text{H}_2$. The differences between the heats of adsorption from H on a series of transition metals would then follow D_MH .¹⁵

(iii) Lastly, the values of $(i_\text{o})_\text{H}$ to $(i_\text{o})_\text{D}$ on Fe (a metal which is with Conway and Bockris' second class, rate-determining $\text{H}^+ + \text{H}_\text{ads} + \text{e}_\text{o}^- \longrightarrow \text{H}_2$) are not consistent with this reaction. However the position of this metal in the $\log i_\text{o} - \Delta H$ graph, compared with the $\log i_\text{o} - D_\text{MH}$ line for Hg, Pb and Tl, makes it possible that Fe is a proton discharge case.¹⁵

The Conway and Bockris view of 1957 makes a consistent picture of the relative efficacy of catalysts for the h.e.r. and one for which the difficulties are not insuperable. It has been developed by others.⁹⁵ The next approximation should take into account the effect of interactions between H atoms on the surface and deal with the question of tunnelling.

2. Hydrocarbons

Facts concerning ethylene oxidation on Pt, Ir, Rh, Au and Pd¹³ are summarized in Table XII. The relative rates are shown in Fig. 21.

Group I (Pt, Ir, Rh) oxidizes ethylene to CO_2 quantitatively, shows a Tafel slope of $2RT/F$ and has $(\frac{\partial \ln i}{\partial \text{pH}})_E \simeq \alpha$. The Group III (Au, Pd) gives incomplete oxidation, and exhibits a Tafel slope nearer to RT/F than to $2RT/F$ and has $(\frac{\partial \ln i}{\partial \text{pH}})_E = 0$.

For the first Group, the M-C bonds have a strength higher by $20 \pm 5 \text{ kcal mole}^{-1}$ from that of Group II. Incomplete oxidation with Au and Pd can be more easily understood, than with Pt, Ir and Rh, because the intermediate products would have a higher rate of desorption.

Interpretation of the relative rates of Au and Pd is difficult because hitherto no mechanism study on these metals has been made. Rudimentary ideas on the mechanism, namely from the current-potential and the pressure effect (positive) suggest a mechanism of the type:



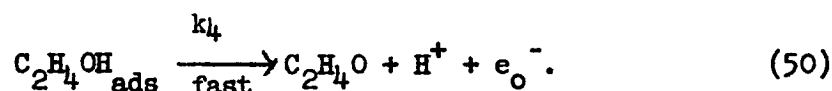
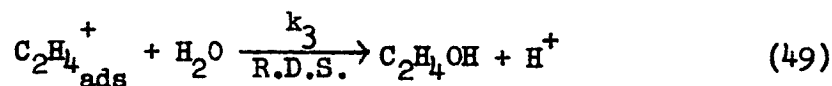
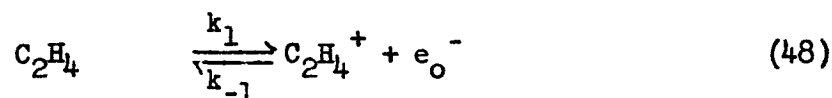
TABLE XII

ETHYLENE OXIDATION AND CHARACTERISTIC PROPERTIES OF THE METALS

Reaction product	"Chemical" reaction rate at p.z.c. Amp/cm ²	pH dependence $\left(\frac{dE}{dpH}\right)_i$	Tafel slope $\left(\frac{dE}{2.3d\log i}\right)$ mV	Lattice parameter a_0 [Å] (from 100) (hydrogen scale)	Potential of zero charge $\Delta\phi$ p.z.c. (hydrogen scale)	Vacant d orbitals per atom (from 98) (from 32)	Heat of Sublimation I_s (kcal mole ⁻¹)
Platinum	1×10^{-7}	70	160	c.f.c. 3.914	+30 99	.55	135
Iridium	1×10^{-11}	75	132	c.f.c. 3.823	+0.05+100 ⁺	1.5	165
Rhodium	5×10^{-11}	70	155	c.f.c. 3.794	0.05+100 ⁺	1.5	138
Gold	1×10^{-11}	0	72	c.f.c. 4.070	+30 100-101	0	84
Palladium	7×10^{-10}	0	80-110	c.f.c. 3.879	+25 ¹⁰⁰	.55	91

* potential of zero charge (formerly: e.c.m.)

+ calculated eq. () using electronic work functions 97



If this type of mechanism is valid for the major contribution to the reaction, the heat of activation will be determined primarily by the heat of adsorption of C_2H_4^+ and CH_3CHO ; as also by the thermionic work function. Very roughly, one can suppose that the heat of adsorption of C_2H_4^+ and CH_3CHO do not greatly differ for a given metal and hence in a first approximation, the influence of the M-C bond strength can be neglected. The work function effect remains. The experimental rates of water discharge at the potentials of zero charge are about 10^2 and the theoretical about 10^3 .

On Pt, Ir and Rh, the rate-determining step is probably water discharge, $\text{H}_2\text{O} \longrightarrow \text{OH}_{\text{ads}} + \text{H}^+ + e_o^-$. The heat of adsorption and work function would be the main metal-dependent parameters in determining the rate. But the OH and H_2O bonding, - and differences thereof on each metal, - would tend to cancel. Hence, one might expect again principally a work function dependence. The observed and expected trends are consistent, though the agreement is hardly better than qualitative.

It is a feature of the reactions of the oxidation of hydrocarbons that the coverage with oxide is important and shuts off the reaction (by its formation of an oxide layer) at various characteristic paths (see Fig. 20 and 6).

VI: NEEDED TRENDS IN RESEARCH

It was stressed early in this paper that knowledge of the theory of electro-catalysis is at a rudimentary level. Some leading doubts in the present position are herewith outlined.

(1) Adsorption and interactions within adsorbed layers:

Much more knowledge of the dependence of the adsorption of organic compounds on potential, and upon their own structure and that of the solid metal, is needed than that given in the initial papers by Bockris and Swinkels.⁴⁷

Similarly, the O and H adsorption position is restricted in available knowledge almost to the noble metals. The importance of knowledge of the potential dependence of this adsorption is illustrated by Dahms and Bockris¹³ results on the inhibition of the ethylene oxidation rate when the adsorbed O is replaced by an oxide. The relative rates of the same electrochemical reaction on a metal and a monolayer of its oxide are not known. A tentative calculation²⁷ for water discharge onto bare and oxide covered Pt yielded the ratio of $\frac{K_{P+}}{K_{P+O}} \approx 10^8$.

Lastly, the equations of state for adsorbed layers on electrodes are unexamined, although a beginning in this direction has been given by Blomgren, Bockris and Jesch⁴⁴. The importance of such work is exemplified by the findings of Conway and Gileadi:⁹⁶ the existence of a sufficiently large interaction between the particles in the final state of a charge transfer reaction causes a change in the interpretation of the mechanism on the basis of the slope of the Tafel line, and reaction orders.

(2) Path and rate-determining step:

The work to date is preliminary and needs not only extension but particularly attack by alternative methods for verification. In this respect the interpretation of transient studies is desirable. Tafel slope, pH, and pressure effects, taken with a knowledge of θ_{organic} and θ_0 in the organic oxidation reactions, contribute substantially to mechanism elucidation.

Although the study of a half dozen hydrocarbon oxidation reactions by these methods would be helpful, it would still not allow a solid theory of electrocatalysis of hydrocarbon oxidation (a central topic from the view point of electrochemical energy conversion) until information on a large number of materials, rationally chosen to evaluate, e.g., the effect of change of lattice parameter; the influence of crystal face orientation; the effect of the d band characteristics; and that of work function. It is desirable to have information, therefore, on a large number of systems, of which the following appears to represent the significant groups: (a) the noble metals; (b) alloys of the noble metals and Group Ib; (c) non-noble metals in alkaline solution; (d) noble metals containing small quantities of materials exhibiting redox properties, e.g., Mo; (e) the semiconducting surfaces, e.g., carbides and borides.

Attention to variation of the rate with time at constant potential is of great importance, not only from the point of view of energy conversion (cf. the possibility of maintaining the high current density which exists initially after charging has terminated) but because knowledge of the mechanism of the variation with time is important in mechanism

interpretation. For example, in ethylene oxidation, the choice of H_2O , rather than C_2H_4 , as the source of the charge depends upon the observation of the decrease of current with increase of C_2H_4 concentration in steady state. This is an acceptable conclusion, however, only if it can be satisfactorily proved that it is not a product of a branching reaction which poisons the electrode.

(3) Theoretical

Several basic aspects of the theory of electrode kinetics are uncertain.

(a) Theory of β : Is charge transfer describable in terms of classical equations, or is there a tunnelling of electrons over the small distances involved?

(b) Work Function: Which work function is effective and how is the vacuum-measured value dependent on the water and organic molecule adsorption?

(c) Electronic Structure of adsorbed organic compounds: Detailed descriptions of bonding in terms of molecular orbitals offer attractions for predictions concerning the rates of charge transfer reactions at electrodes. Such considerations have been neglected so far in the theory of organic electrochemical reactions.

(d) Structure of the electric double layer in the presence of adsorbed, reacting entities: How do the water dipoles in the double layer before additions of the organic molecule depend on potential and on the organic adsorption? Where is the reacting entity, outside a layer of adsorbed water or not? To what extent does our fairly good

knowledge of the double layer structure on polarizable interfaces of Hg in aqueous solutions of simple inorganic ions apply to solid electrodes in the presence of organic molecules? What effect has the breakdown of the polarizable character of the double layer during reaction upon the structural model?

Electrochemistry stands at an early stage in the investigation of electro catalysis. Progress in research in this field would make available energy conversion methods of wide applicability.

Acknowledgements: The authors are grateful for help of discussion with their colleagues in the Electrochemistry Laboratory of the University of Pennsylvania; and in particular to Drs. S. Srinivasan, A. Damjanovic, E. Gileadi, B. Rao and A. Dey. They wish to acknowledge with thanks discussion with Dr. Alan Day, of the John Harrison Laboratory of Chemistry, University of Pennsylvania, of the electronic aspects of the hydrocarbon oxidation mechanisms. They are grateful for the support of the National Aeronautical and Space Administration; to the Air Force (Wright Patterson); and to the United Aircraft Company, for support.

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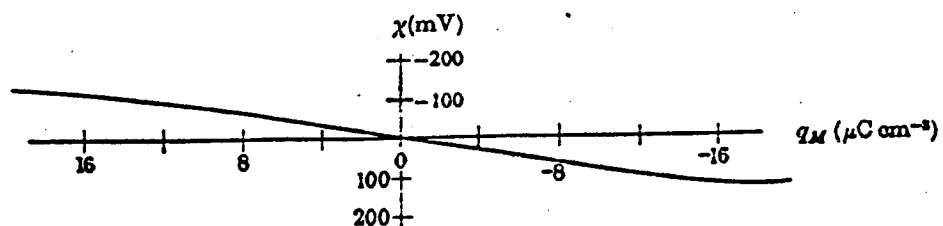


FIG.1 The χ potential at the metal water interface, taking into account the constants for lateral interaction.

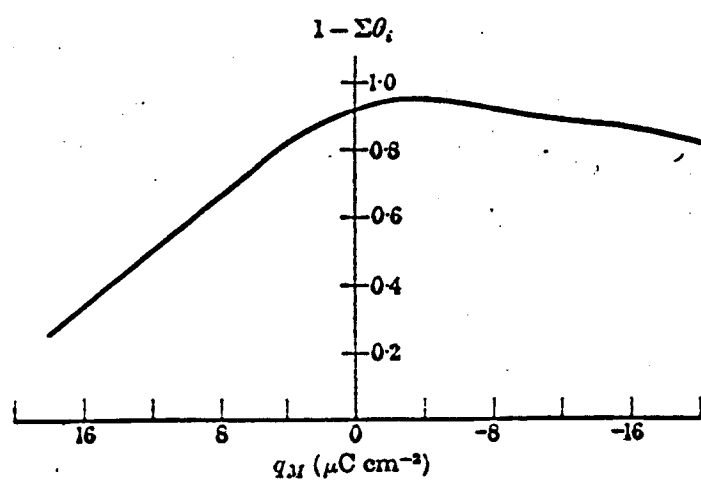


FIG.2 Fraction of the surface not covered with ions in 0.1 NHCl as a function of charge density.

FIG. 3 Current - Potential Relation for Ethylene on Pt and Pt80 Ru20 Alloy.

2N H₂SO₄

120°C

P_{Et} = 1 atm

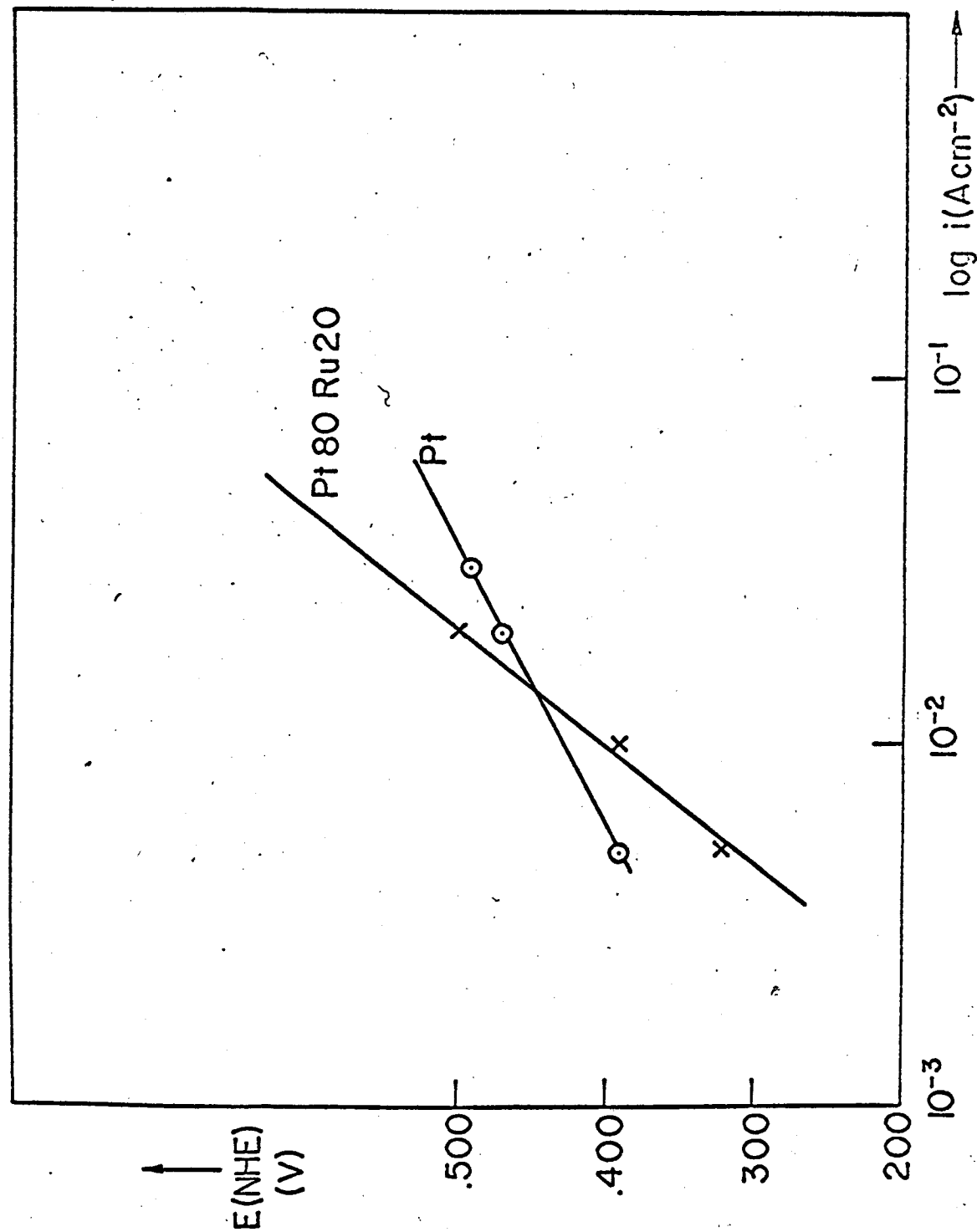


FIG. 4 Limits of the Potential Region of Ethylene Oxidation on Pt and Ir

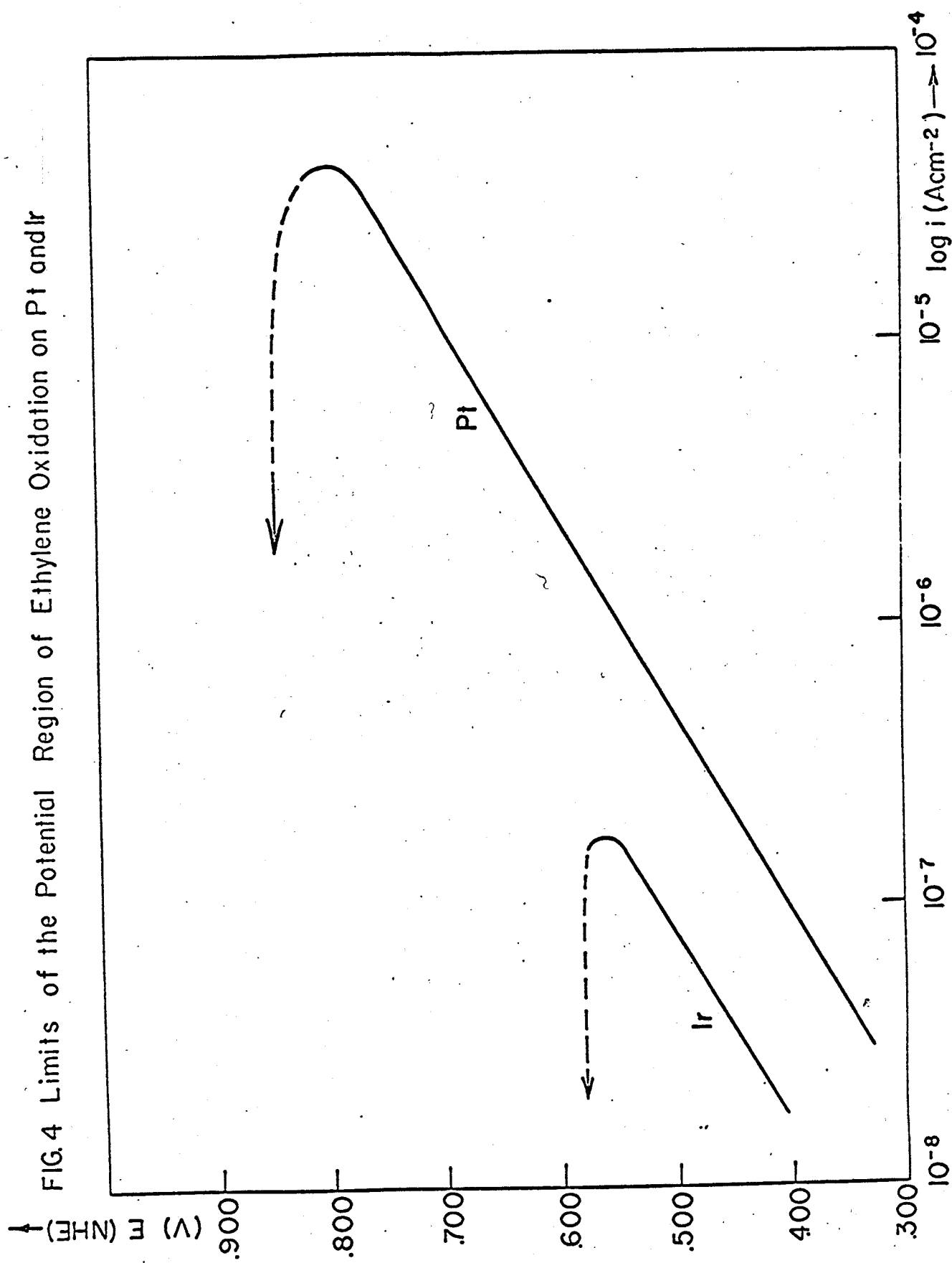
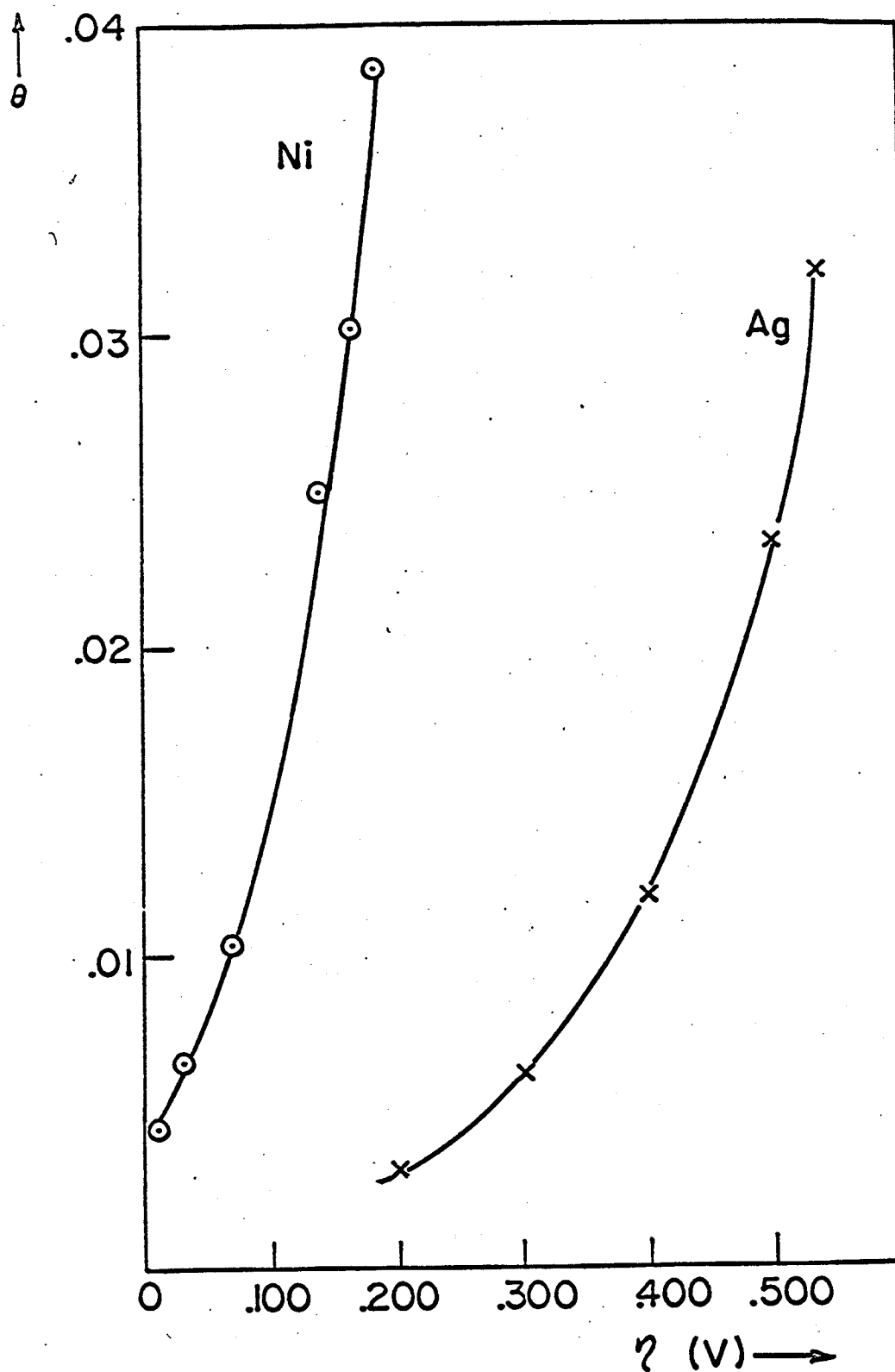


FIG.5 Dependence of the Hydrogen Coverage on Potential for Ni and Ag



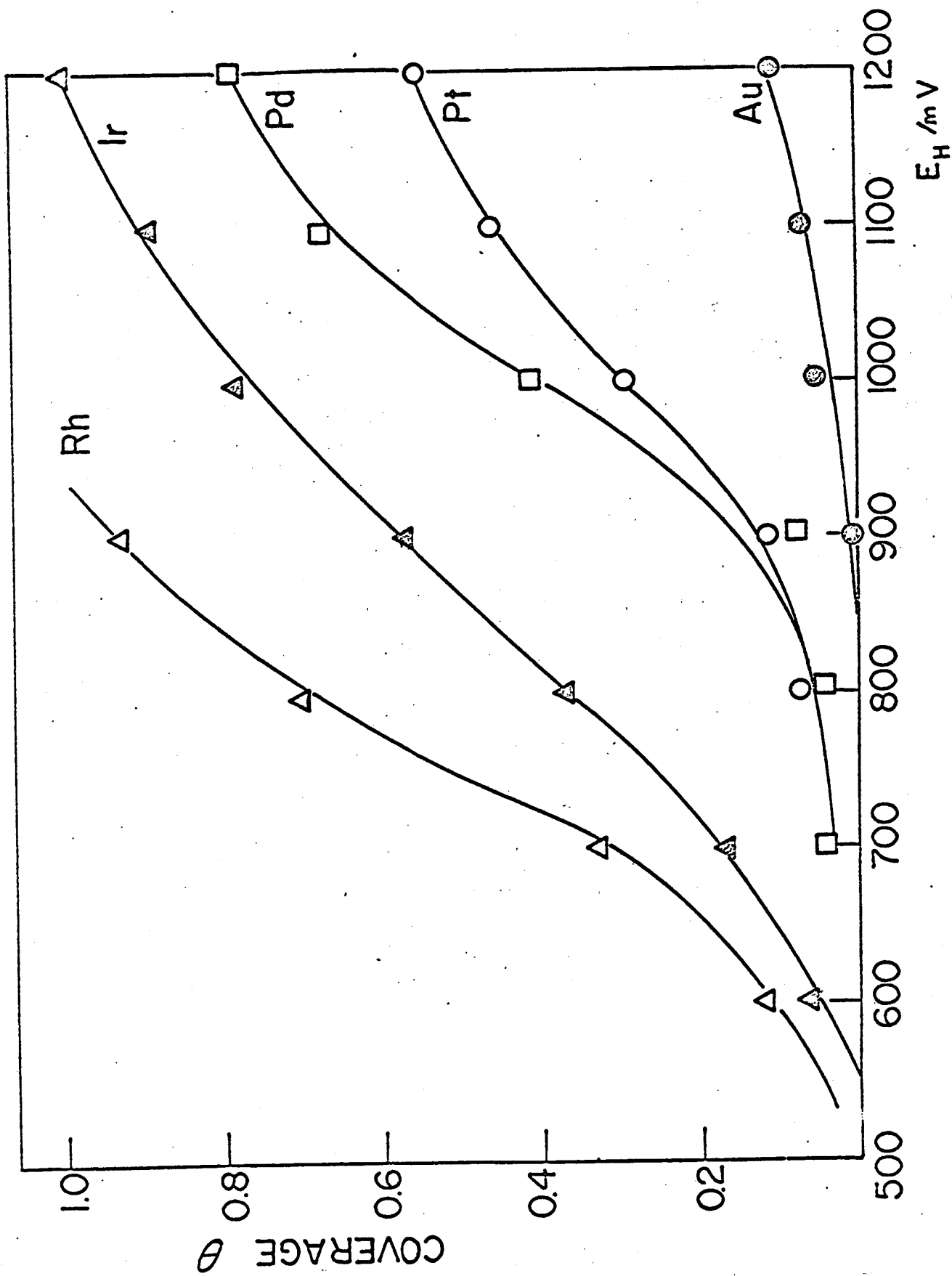


FIG.6 COVERAGE WITH O AS A FUNCTION OF POTENTIAL

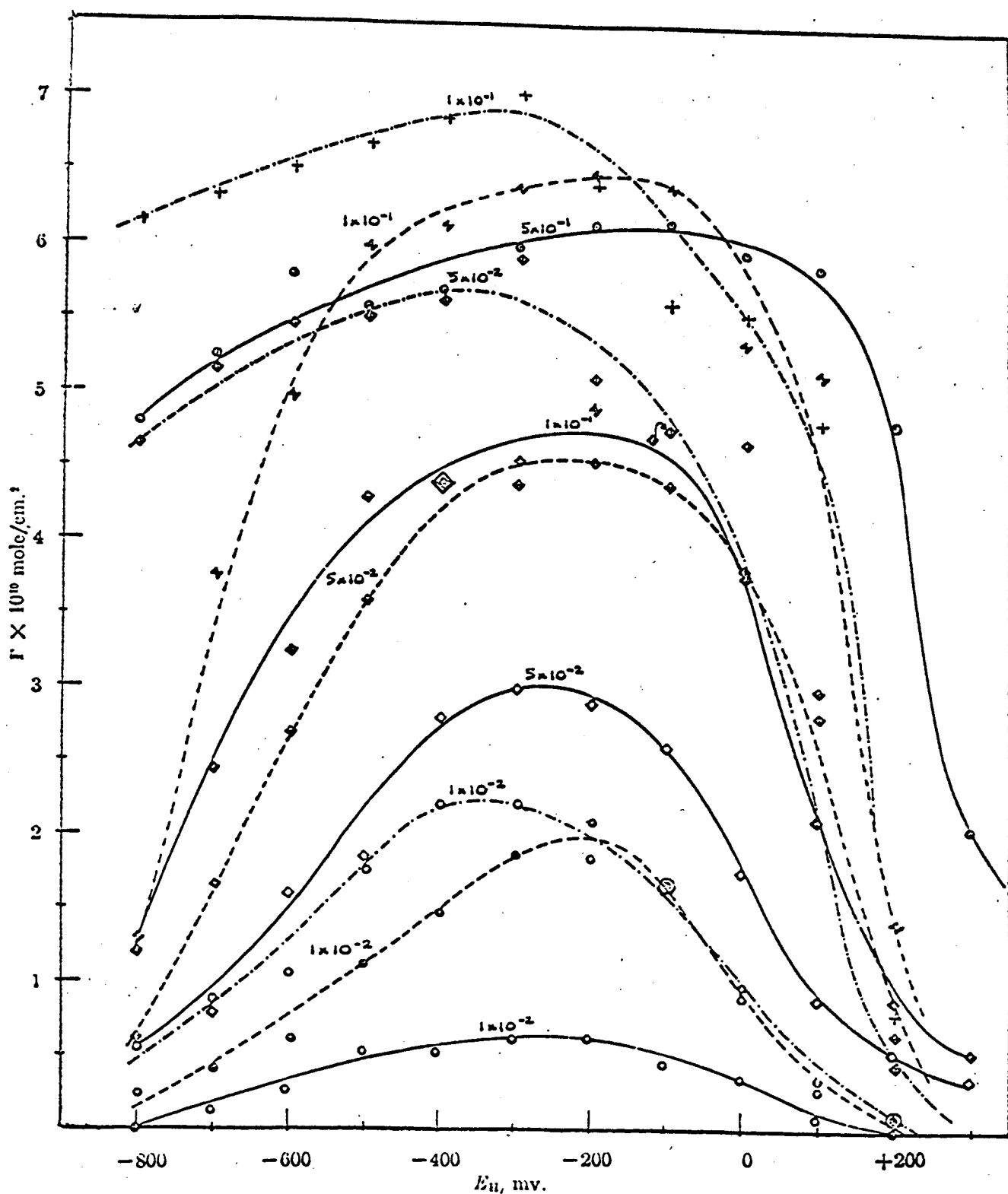


FIG.7 Γ_A as a function of E_H for constant adsorbate concentrations and $\text{CHCl} = 0.1\text{N}$: (a, —) n-butyl alcohol; (b, ---) n-valeric acid; (c, -.-.-) n-valeronitrile. (C_A stated on figure)

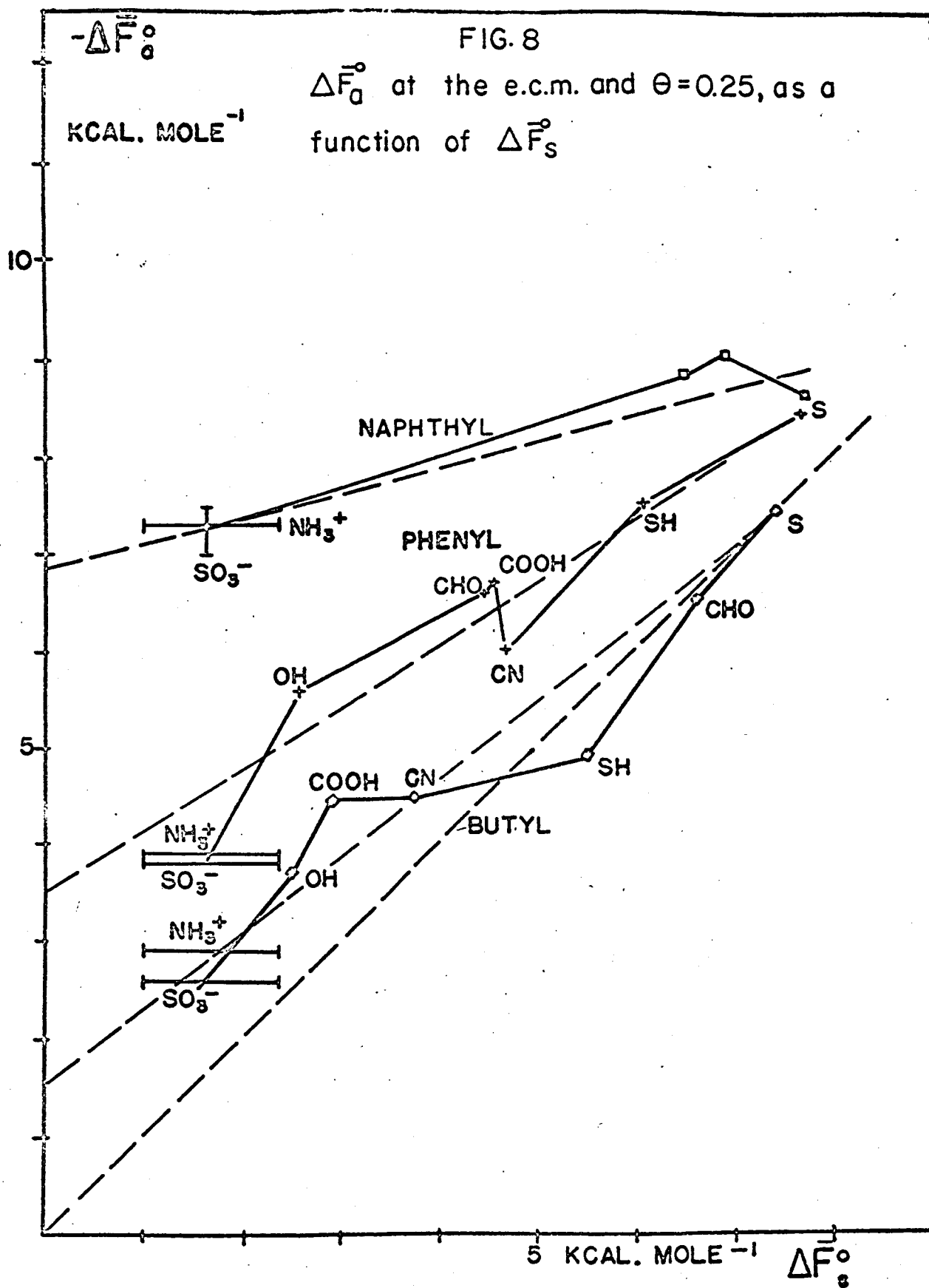


FIG.9 ADSORPTION OF NAPHTHALENE ON NICKEL FROM IN NaClO_4 ; pH = 12

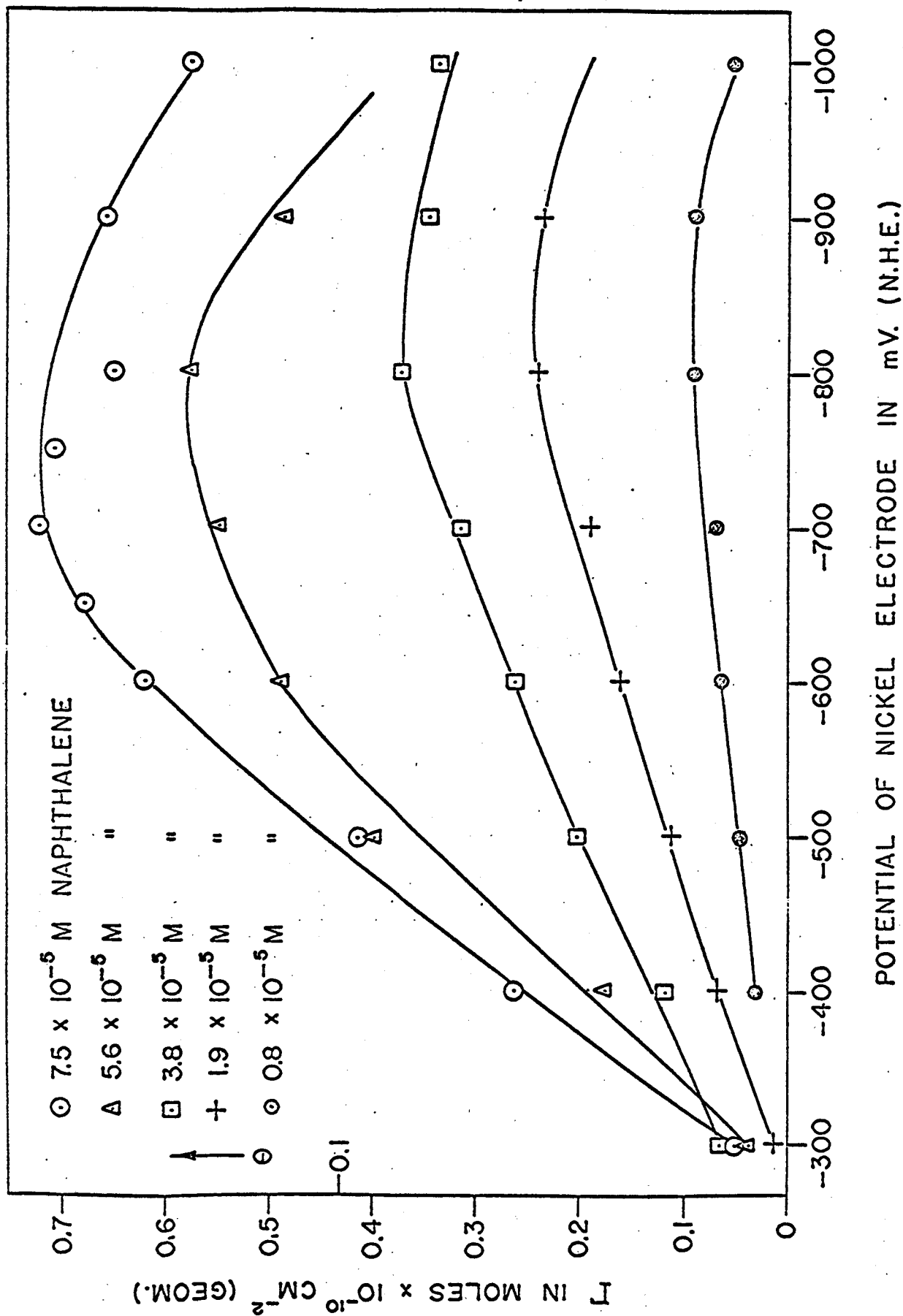


FIG. 10 ADSORPTION OF n-DECYLAMINE ON NICKEL FROM IN Na ClO₄; pH = 12

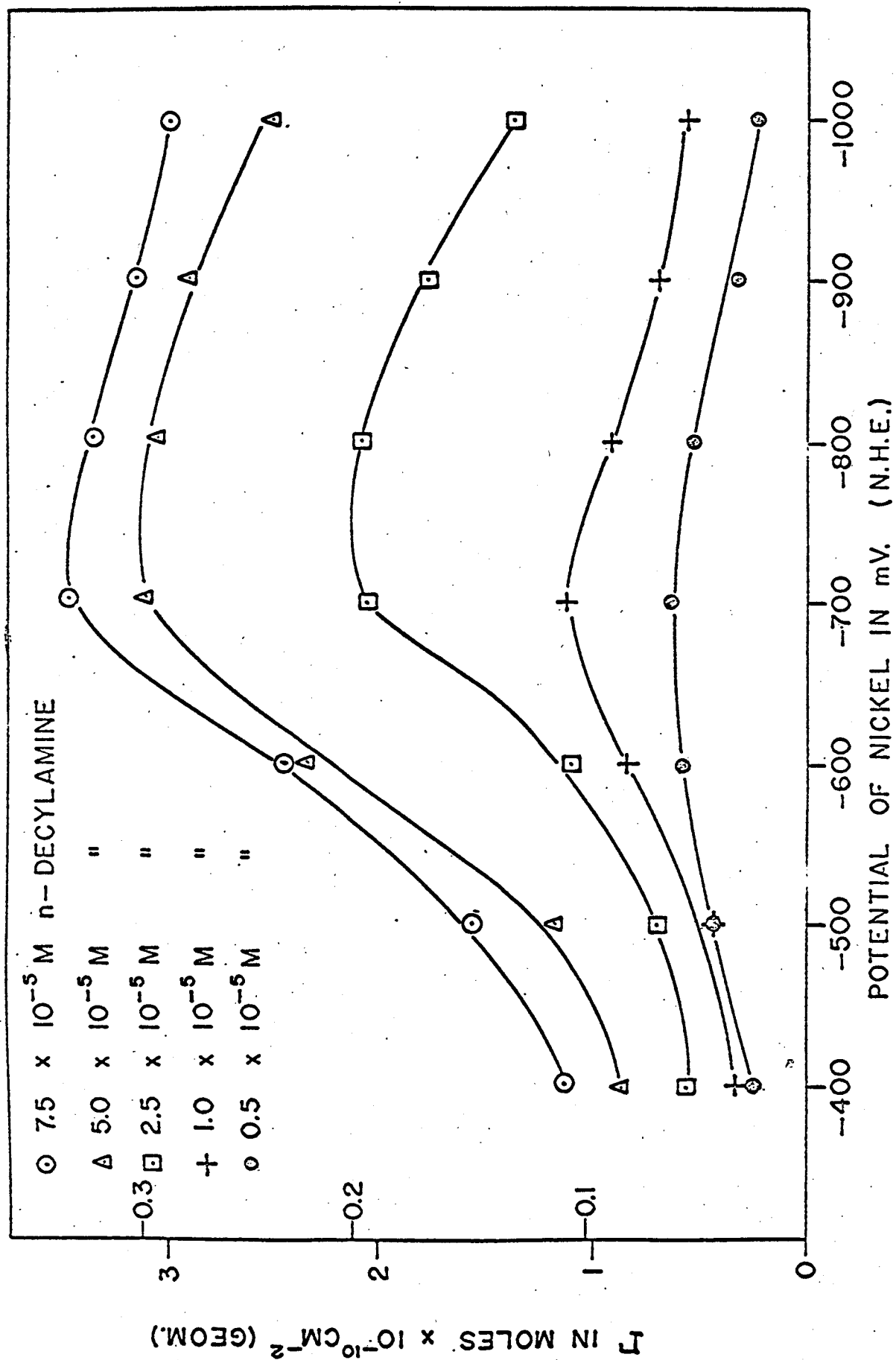


FIG. 11 Adsorption of Naphthalene on Platinum from
 0.9N NaClO_4 ; 0.1N HClO_4 ; 2.5×10^{-6} M Naphthalene

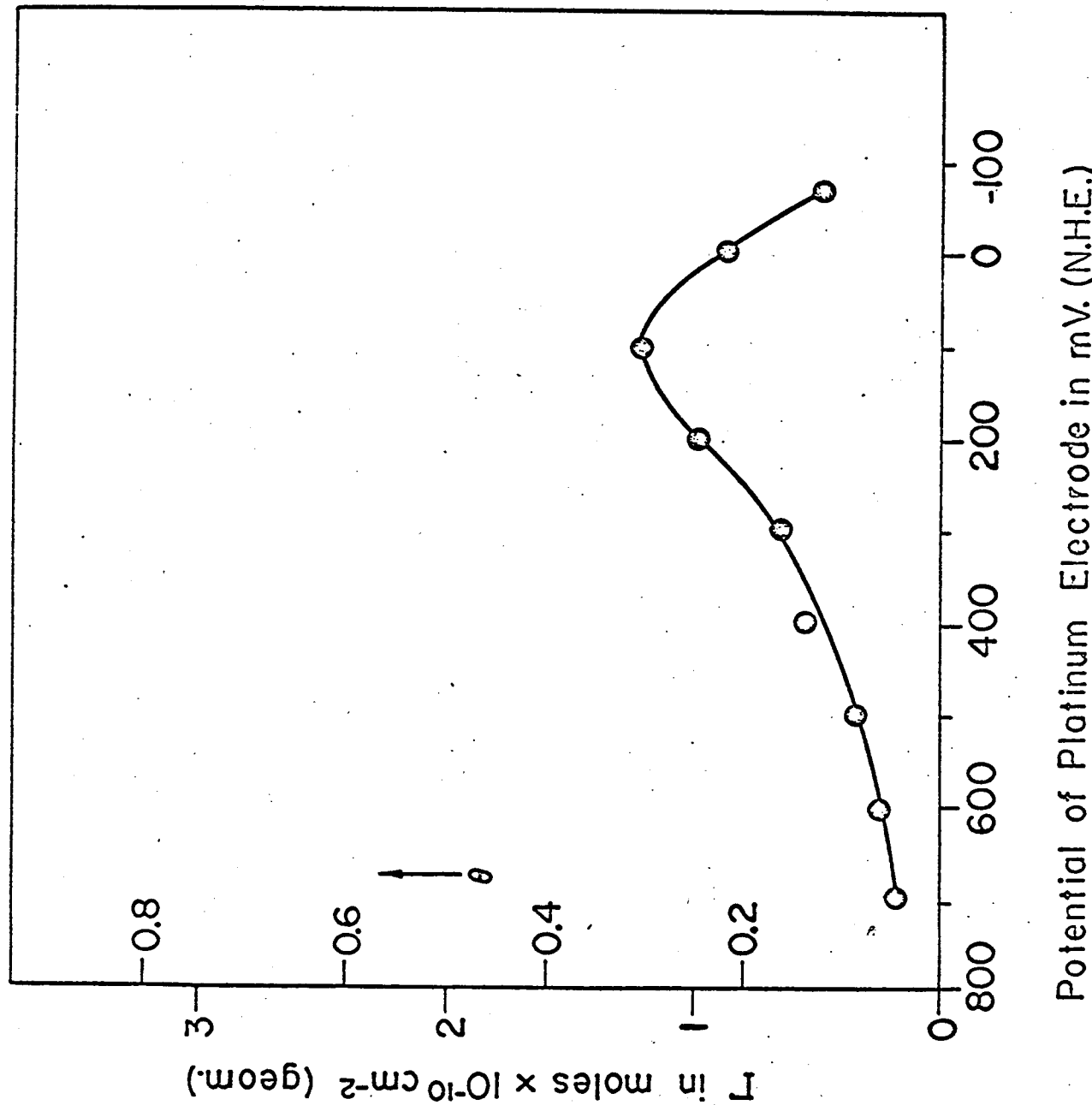


FIG.12 POTENTIAL ENERGY-DISTANCE RELATION FOR WATER DISCHARGE

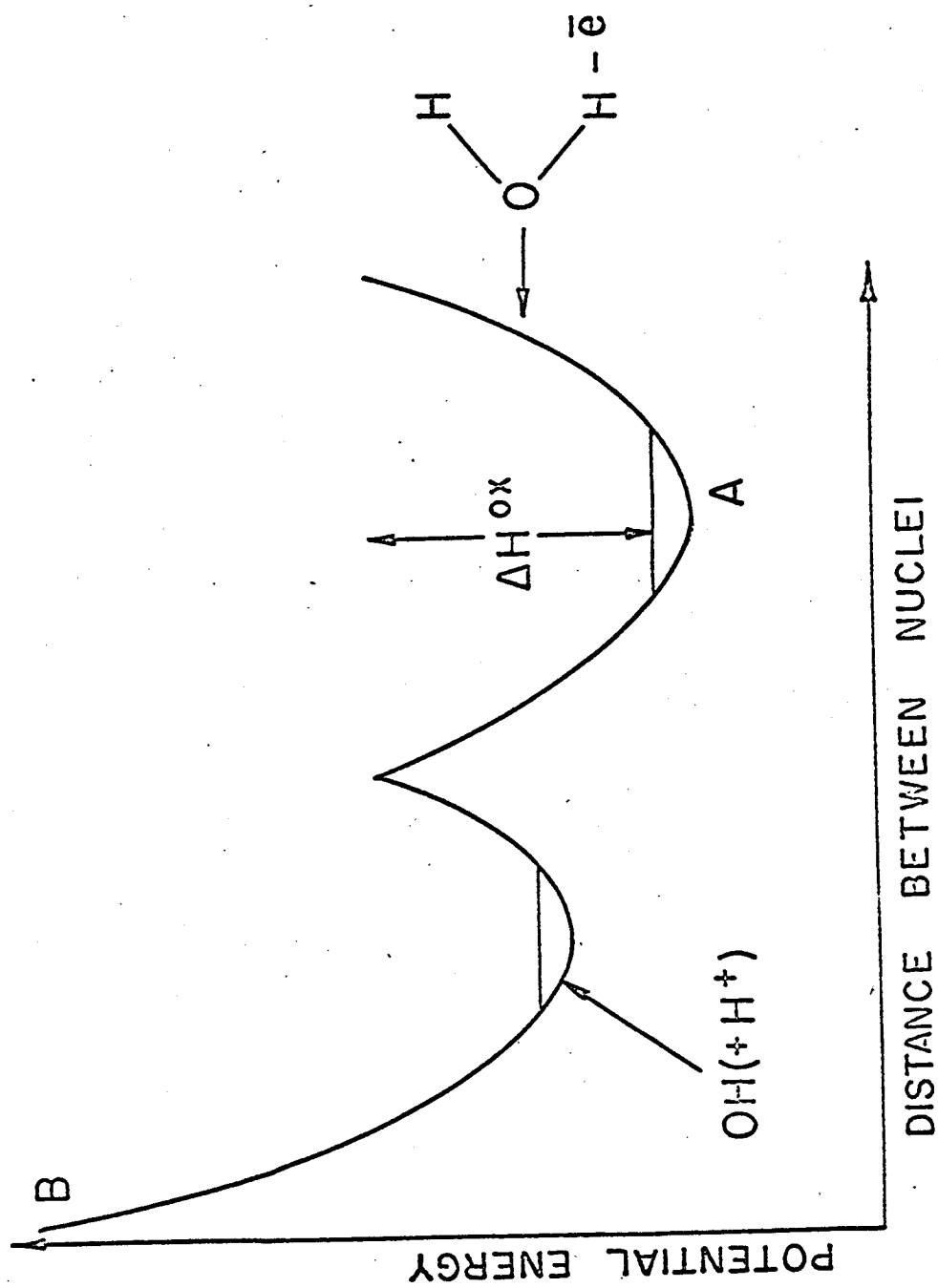
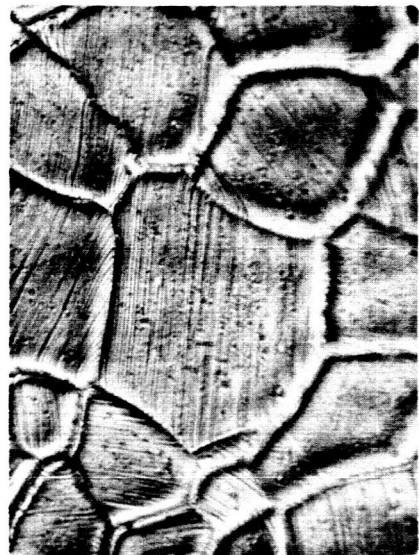
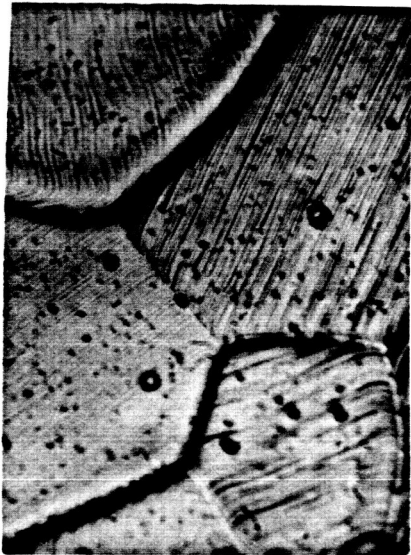
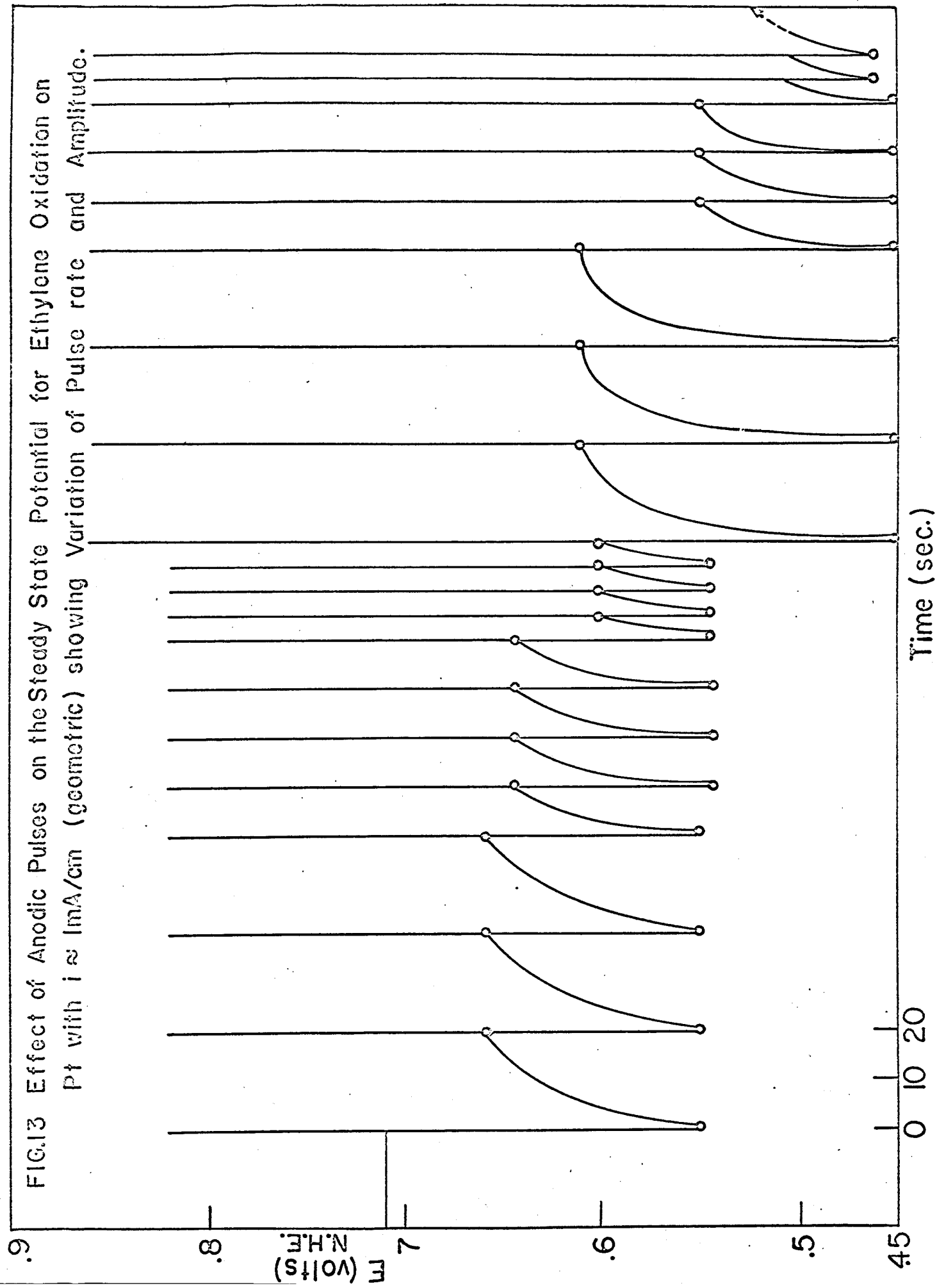


FIG.13





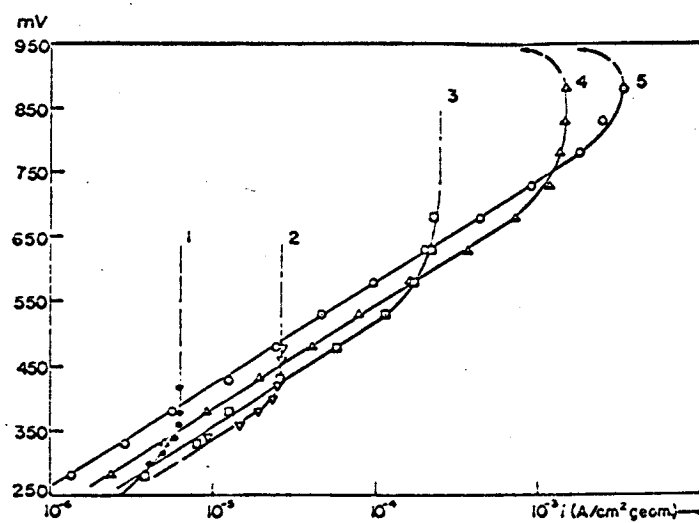


FIG.14 Current potential relation (pH .5) as a function of ethylene partial pressure: (1) $P_E = 10^{-4}$ atm, (2) 10^{-3} atm, (3) 10^{-2} atm, (4) 10^{-1} atm, (5) 1 atm

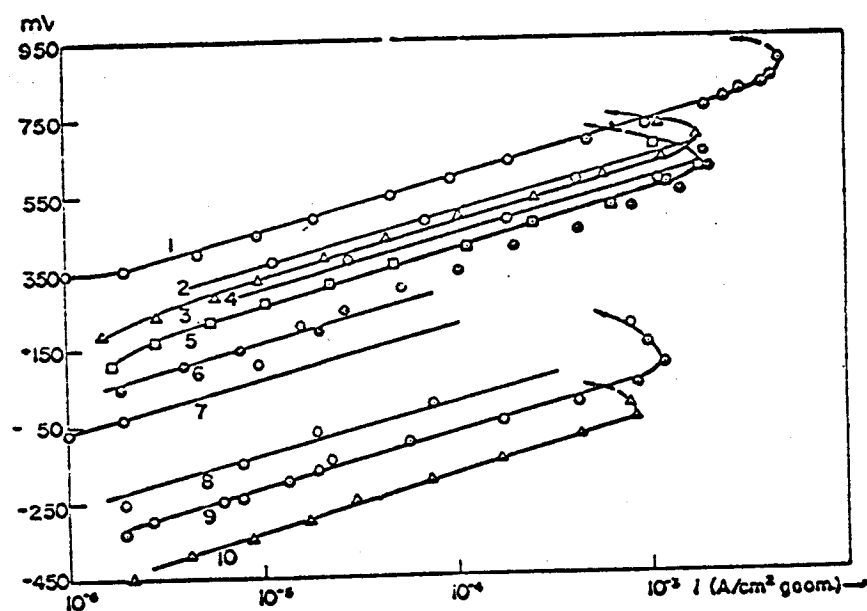


FIG.15. Current-potential relation ($P_E = I \text{ at } m$) as a function of pH:
 (1) 0.5, (2) 1.9, (3) 2.3, (4) 2.9, (5) 3.45, (6) 5.6, (7) 6.5, (8) 9.8, (9) 10.8,
 (10) 12.5

FIG.16 CURRENT AS A FUNCTION OF ETHYLENE PARTIAL PRESSURE AT CONSTANT POTENTIAL: (1) 0.38V, (2) 0.43V, (3) 0.48V, (4) 0.53V.

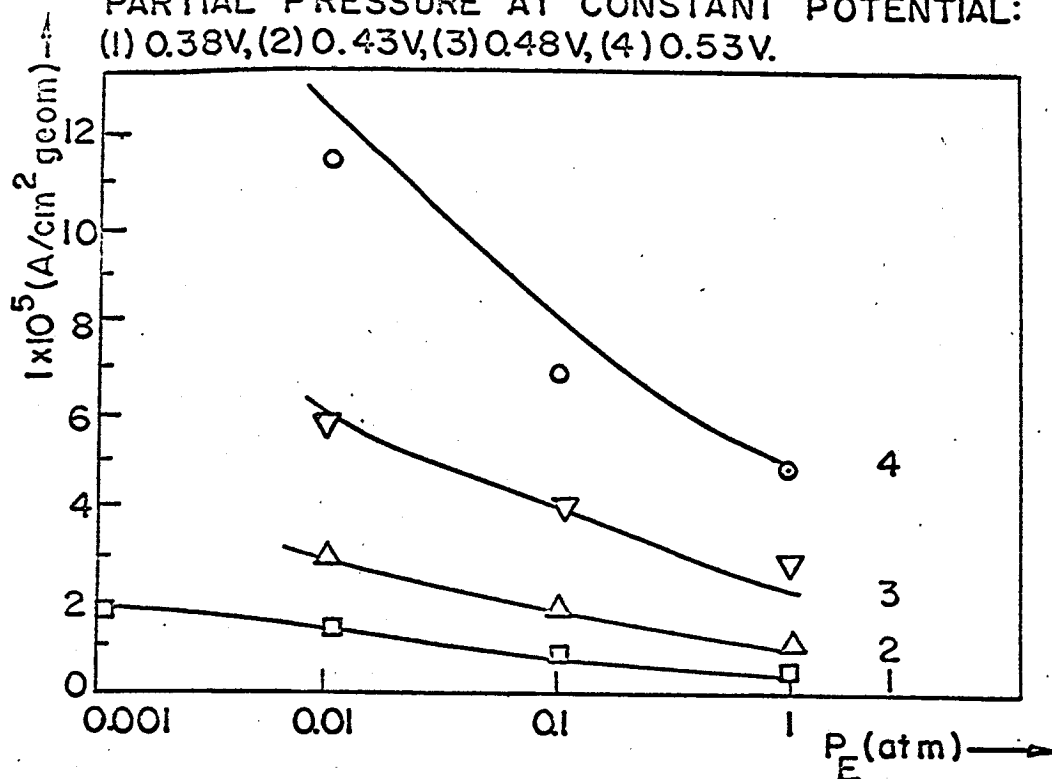
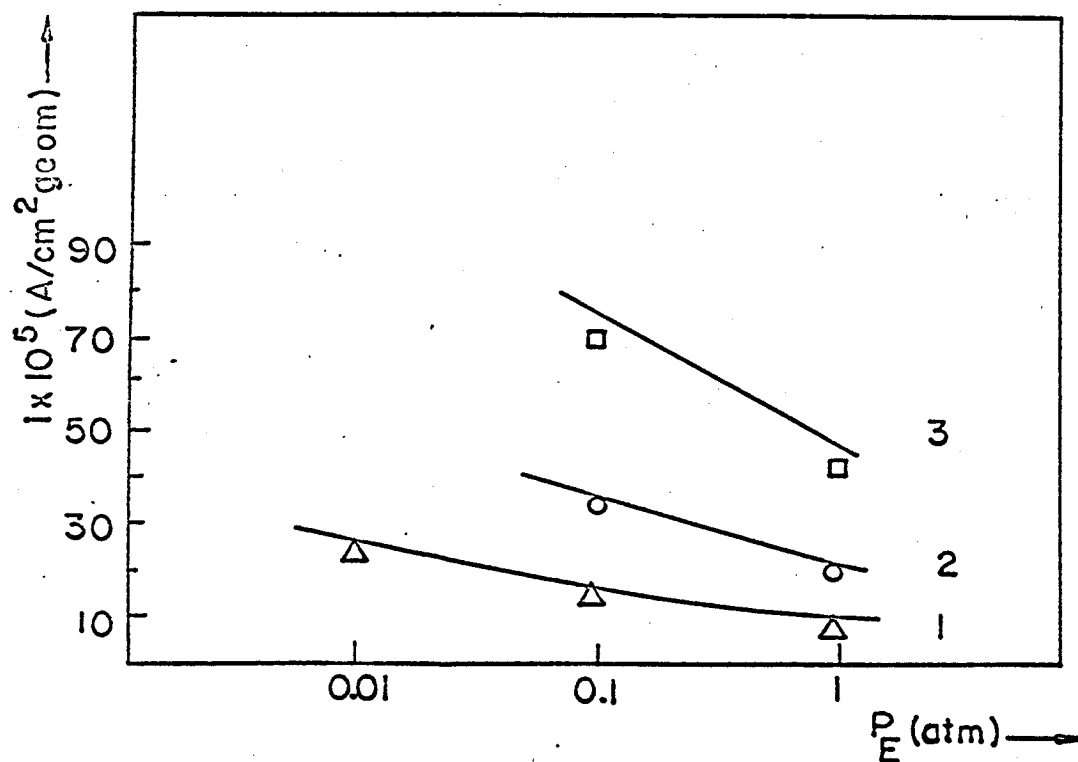


FIG.16a SAME AS 16 (1) 0.58V, (2) 0.63V, (3) 0.68V.



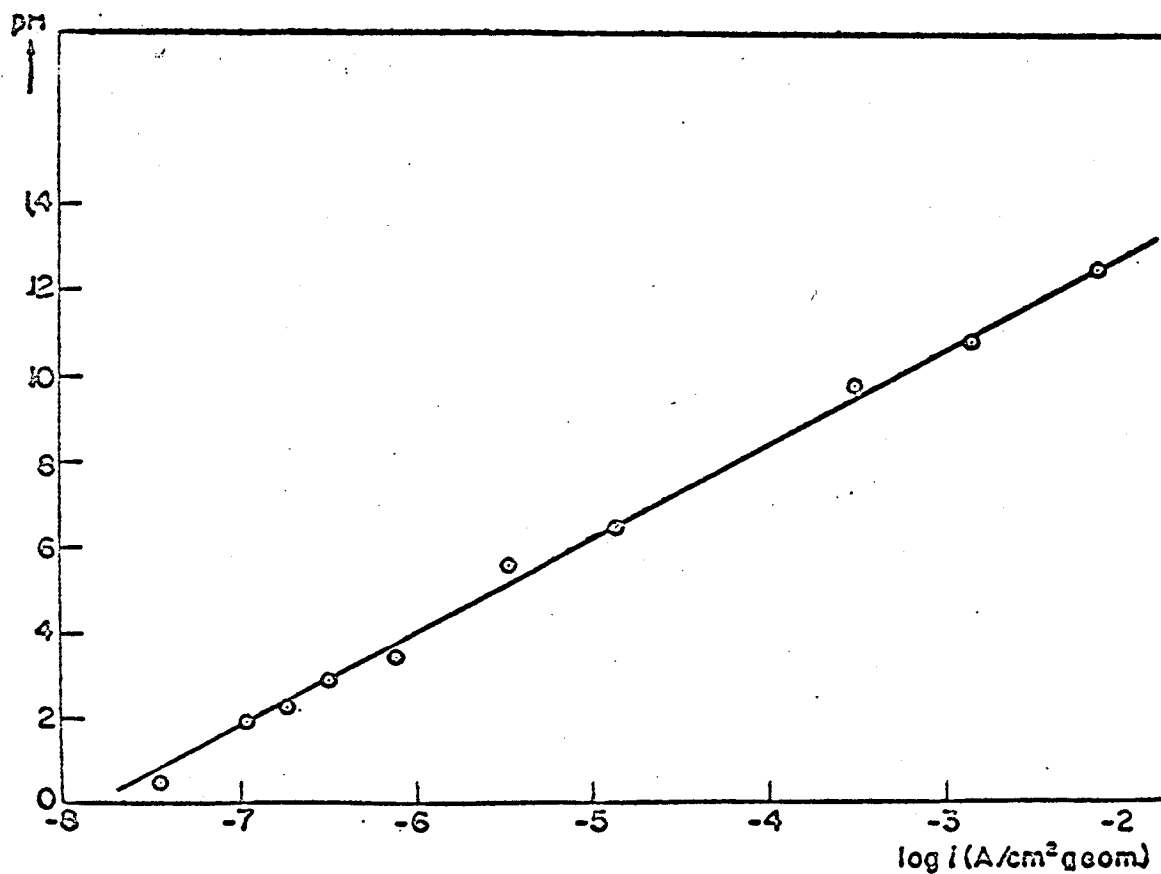


FIG.17 Current ($V = .100V$) as a function of pH.

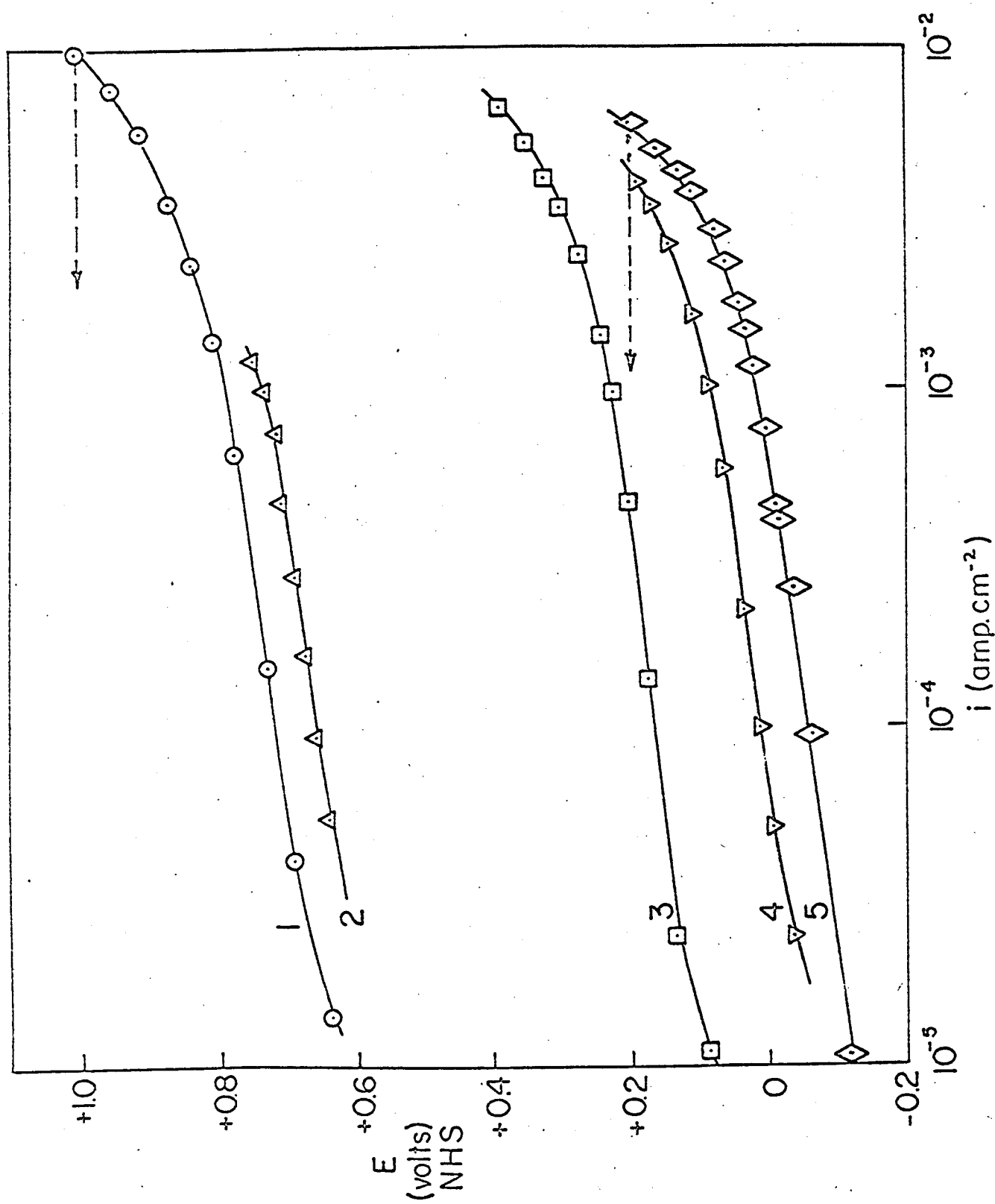


FIG.18 Current Potential Relation in Acetylene Oxidation pH= (1) 0.3,(2)1.2, (3)8.7, (4)11.9 (5)12.6

FIG. 19 Current as a Function of pH at Constant Potential
(Oxidation of Acetylene on Pt Black)

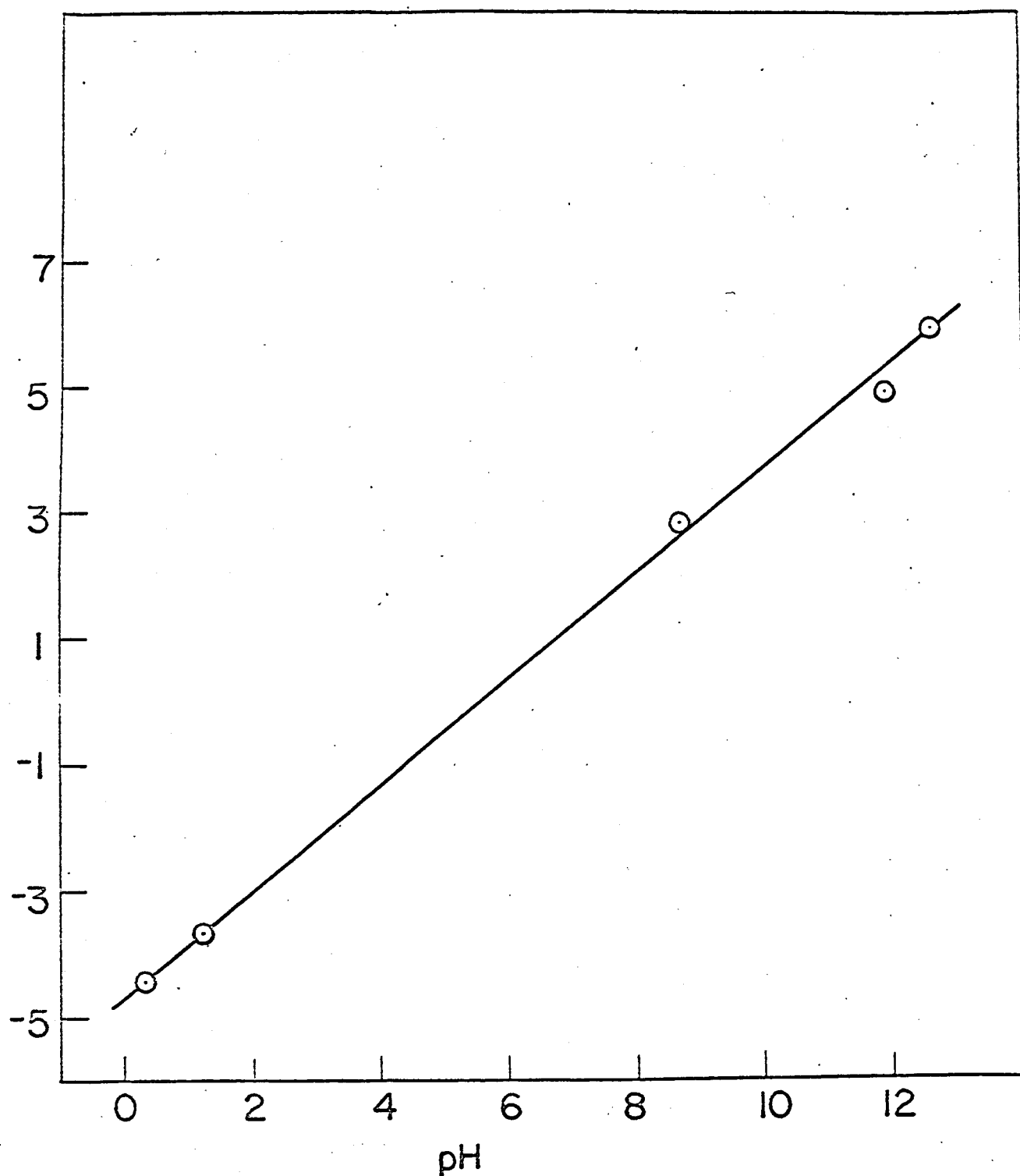


FIG.20 Theoretical Dependence of Current on Acetylene Partial Pressure as a Function of Potential:

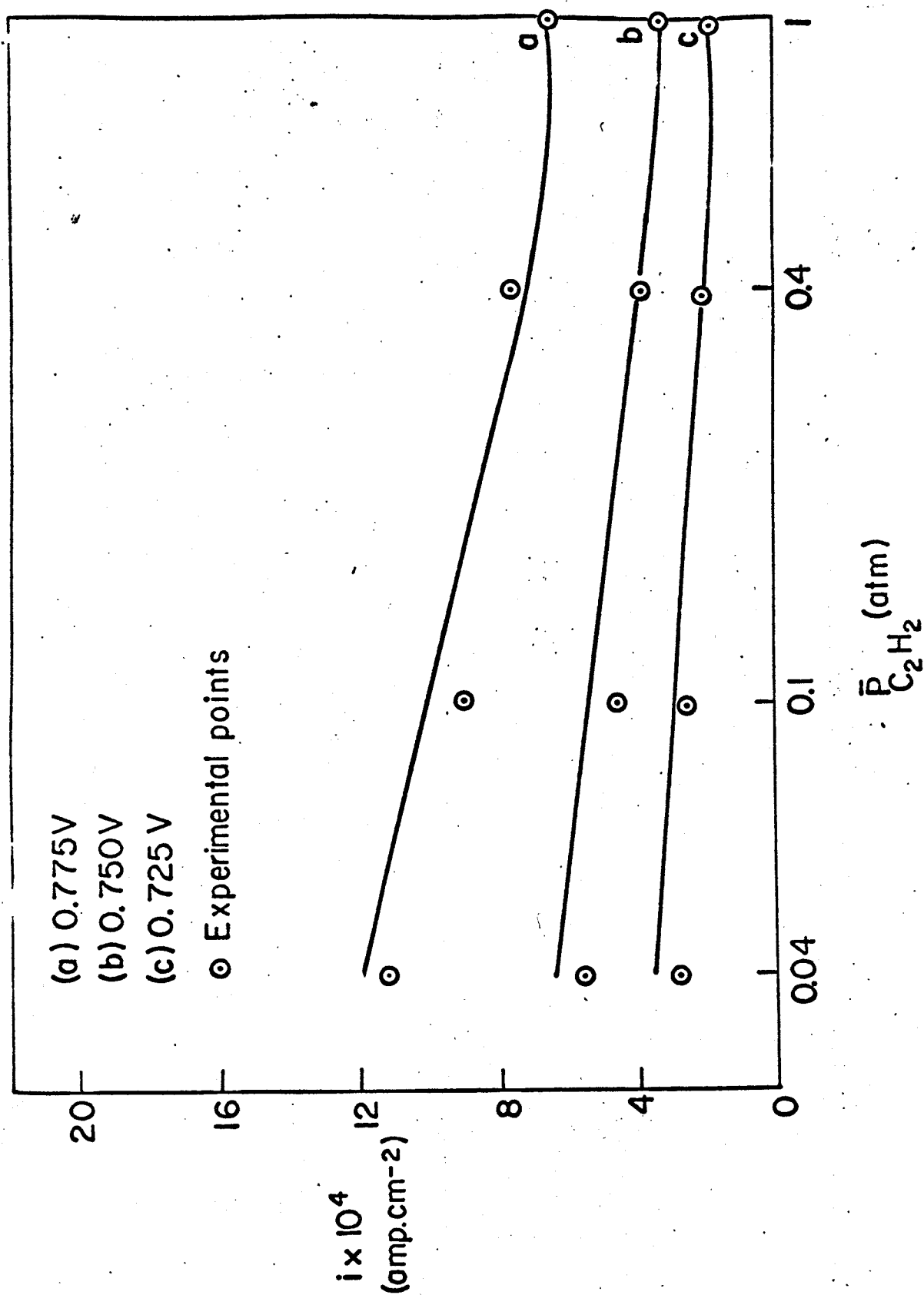
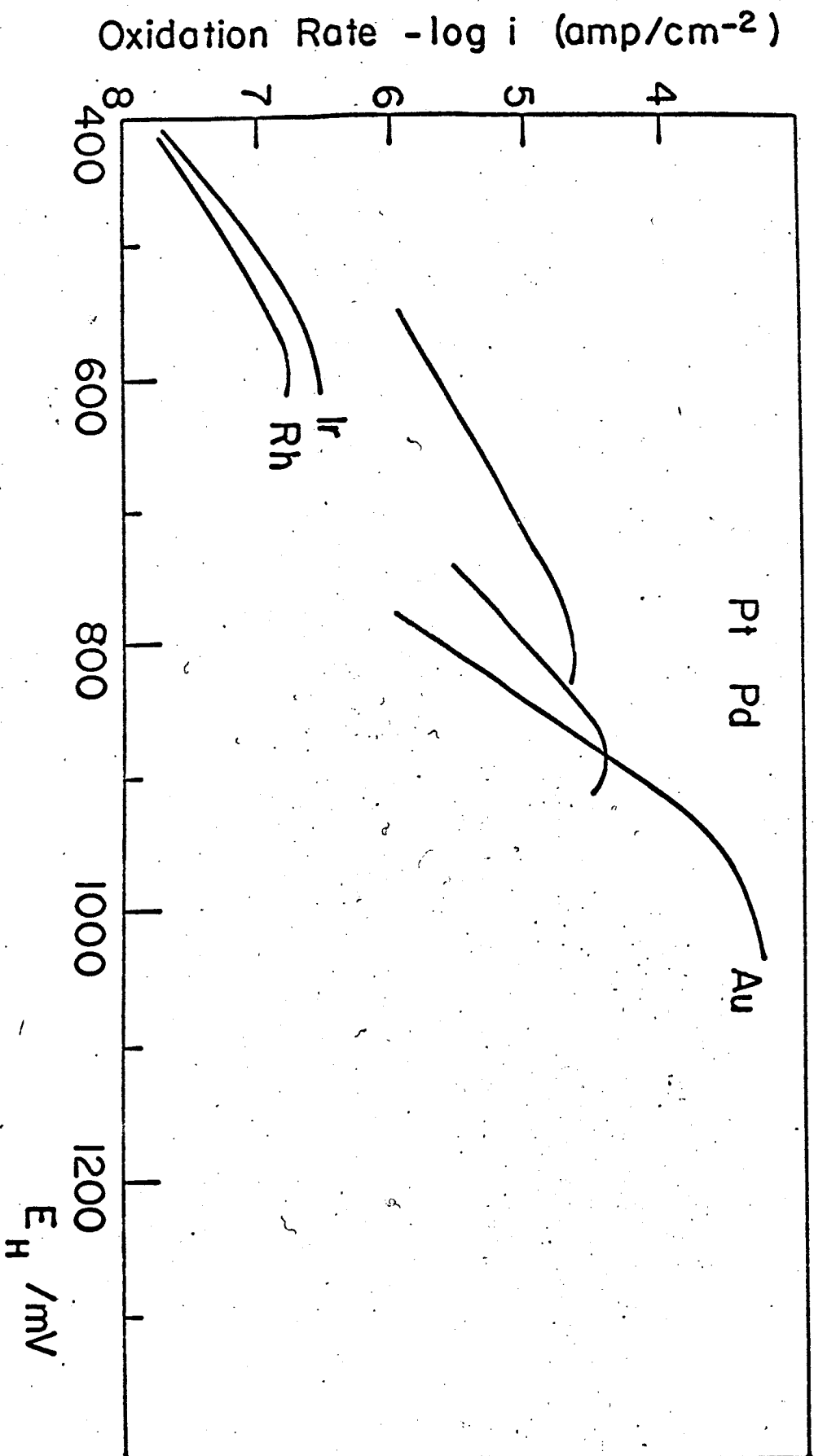


FIG.21 Current Potential Relation for Ethylene Oxidation on Various Noble Metals (80°C, 1N H₂SO₄)



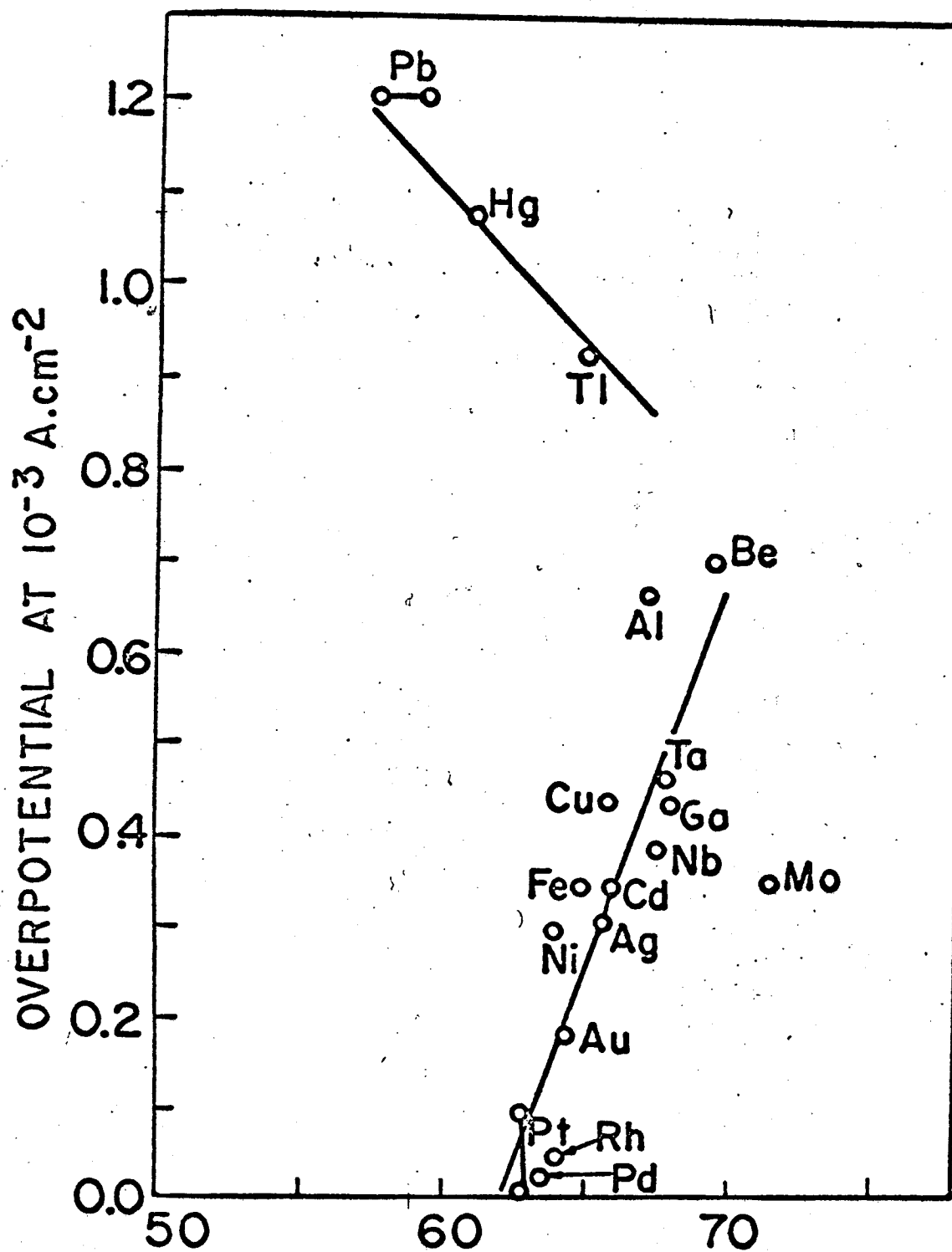


FIG.22 MH- INTERACTION ENERGY PARAMETER
IN Kcal.mole^{-1}

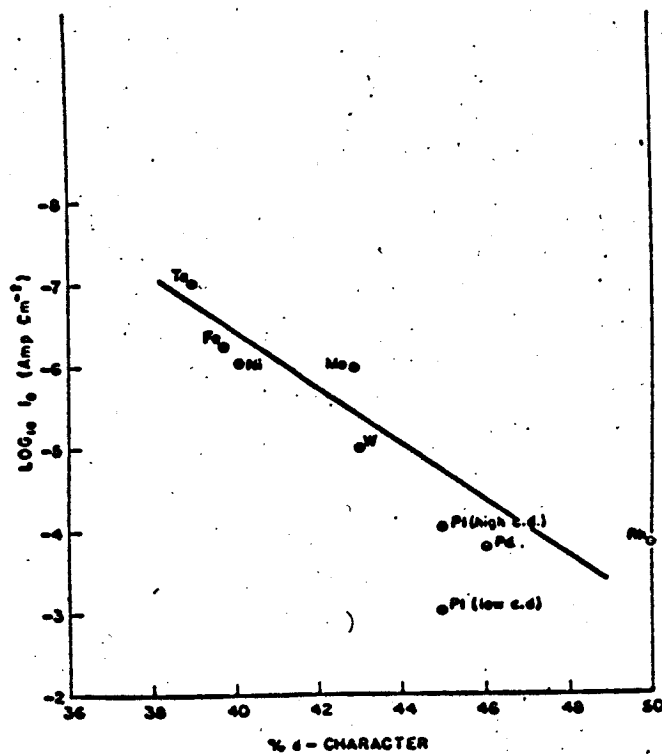


FIG.23 $\text{Log}_{10} i_0$ for the h.e.r. as a function of d character of the metal.

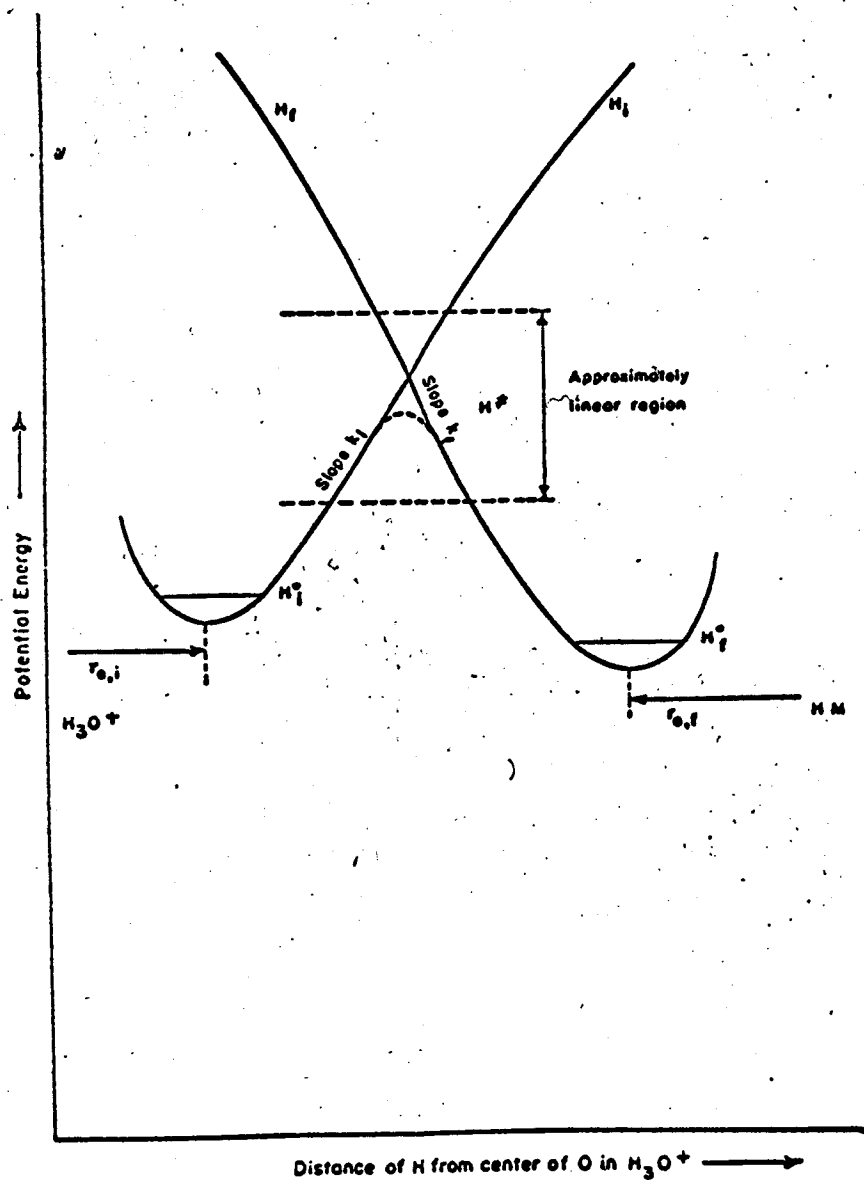


FIG.24 Potential energy diagram for the discharge process
 $H_3O + e^- + M \rightarrow MH + H_2O$

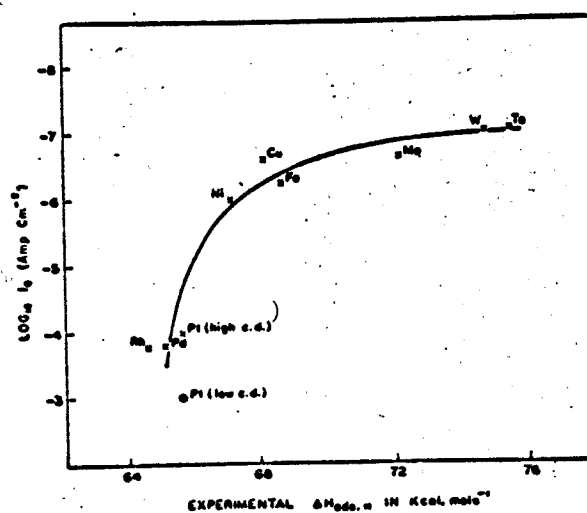


FIG.25 $\text{Log } i_0$ for the h.e.r. at Pt, Pd, Rh, Cu, Ni, Fe, Mo, W, and Ta as a function of the experimental values for heat of adsorption of H at these metals.

A P P E N D I X 2

ELECTROCHEMICAL KINETICS OF PARALLEL REACTIONS

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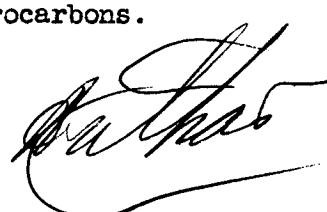
ABSTRACT

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The electrochemical oxidation of complex molecules (e.g. hydrocarbons) sometimes involves branched reactions. Under these conditions, it is difficult to define a reversible potential and the coulombic efficiencies of product formation may then be potential dependent.

A number of cases of the kinetics of branched reactions of the type $A \rightarrow B \begin{cases} \rightarrow C \\ \rightarrow D \end{cases}$, with step $A \rightarrow B$ rate-determining, are worked out.

It is found that in most cases, the coulombic yields are potential dependent over certain potential regions. The calculated variation of coulombic yields with potential is compared with results obtained in the anodic oxidation of some unsaturated hydrocarbons.



INTRODUCTION

The fundamental quantities which determine the thermodynamic feasibility of a fuel cell system are the free energy ΔG , and the entropy ΔS of the overall cell reaction and these quantities are related to the reversible potential and its first derivatives with respect to temperature. In some electrode reactions, e.g., the anodic oxidation of ethylene, the overall reaction varies with the catalyst¹ and caution has to be taken in respect to the appropriate ΔG and therefore the reversible potential.

Examples of electrochemical reactions in which at least two different products are formed are well known.²⁻⁴ Thus in such cases the electrochemical reaction may be a branched reaction, or it may be preceded, accompanied or followed by chemical reactions in solution.

Consider a branched reaction



where the coulombic yields for the formation of C and D are Q_C and Q_D respectively. When the net current is zero, such a system will set up a mixed potential⁵ which lies between the reversible potentials E_{A-C} and E_{A-D} for the two overall reactions. A single reversible potential cannot be defined for such a system, particularly when the coulombic yield Q_C and Q_D are potential dependent.

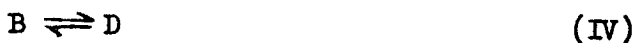
In the treatment below we consider a reaction scheme such as (I), giving rise to two products* and assume that all reactions are

*The extension of this treatment to cases where three or more products are formed is trivial.

activation controlled.*

PARALLEL REACTION SCHEME

Consider an electrochemical reaction of the type (1)



where step II is rate-determining. The rate equations corresponding to these steps will be

$$v_2 = k_2 [A] \exp(\beta_2 z_2 VF/RT) \quad (1)$$

$$v_3 = k_3 [B] \exp(\beta_3 z_3 VF/RT) \quad (2)$$

$$v_{-3} = k_{-3} [C] \exp[-(1 - \beta_3) z_3 VF/RT] \quad (3)$$

$$v_4 = k_4 [B] \exp(\beta_4 z_4 VF/RT) \quad (4)$$

$$v_{-4} = k_{-4} [D] \exp[-(1 - \beta_4) z_4 VF/RT] \quad (5)$$

where k_i , β_i and z_i are the specific chemical rate constant, the symmetry factor and the charge transferred in the i th step, respectively.** V is the metal solution potential difference and the solutions have been assumed to be such that the electrokinetic effects can be neglected.

At steady state we have

$$\frac{d[B]}{dt} = v_2 - (v_3 - v_{-3}) - (v_4 - v_{-4}) = 0 \quad (6)$$

* cf. the work of Bard et al⁶⁻⁸ who considered such effects for diffusion controlled reactions.

** Normally $z = +1$ and it is therefore omitted from the exponential term. In the present treatment $z = +1$ for an electrochemical step and $z = 0$ for a purely chemical step.

hence from equations (1-6) the steady state concentration of $[B]$ at the electrode is

$$[B] = \frac{k_2[A] \exp(\beta_2 z_2 VF/RT) + k_{-3}[C] \exp[-(1-\beta_3)z_3 VF/RT] + k_{-4}[D] \exp[-(1-\beta_4)z_4 VF/RT]}{k_3 \exp(\beta_3 z_3 VF/RT) + k_4 \exp(\beta_4 z_4 VF/RT)} \quad (7)$$

The fractional coulombic yields Q_C and Q_D are defined as

$$Q_C = \frac{i_3 - i_{-3}}{(i_3 - i_{-3}) + (i_4 - i_{-4})} = \frac{n_3(v_3 - v_{-3})}{n_3(v_3 - v_{-3}) + n_4(v_4 - v_{-4})} = \frac{v_3 - v_{-3}}{(v_3 - v_{-3}) + (n_4/n_3)(v_4 - v_{-4})} \quad (8)$$

and similarly

$$Q_D = \frac{v_4 - v_{-4}}{(n_3/n_4)(v_3 - v_{-3}) + (v_4 - v_{-4})} \quad (9)$$

where i_3 and i_4 are the partial currents for the two parallel steps III and IV; and n_3 and n_4 are the total numbers of electrons transferred in the overall reactions $A \rightarrow C$ and $A \rightarrow D$, respectively.

Case 1

We consider first the case when all reverse reactions may be neglected, namely $v_{-3} = v_{-4} = 0$ and derive the various modes of dependence of the rates of the parallel paths on potential and the corresponding coulombic yields.

(a) If steps III and IV are both "chemical" (i.e. $z_3 = z_4 = 0$ and $n_3 = n_4 = z_1$) we have (from equations 2, 4 and 8)

$$Q_C = \frac{v_3}{v_3 + v_4} = \frac{k_3}{k_3 + k_4} \quad (10)$$

and similarly

$$Q_D = \frac{v_4}{v_3 + v_4} = \frac{k_4}{k_3 + k_4} \quad (11)$$

Thus the coulombic yields in this case are independent of potential, but will generally be temperature dependent.

(b) If step III is electrochemical but step IV is purely chemical (ie. $z_3 = 1$; $z_4 = 0$; $n_3 = z_2 + z_3 = 2$; $n_4 = z_2 + z_4 = 1$) we have

$$Q_C = \frac{v_3}{v_3 + (n_4/n_3)v_4} = \frac{v_3}{v_3 + v_4/2} = \frac{1}{1 + (k_4/2k_3)\exp(\beta_3 VF/RT)} \quad (12)$$

and

$$Q_D = \frac{v_4}{(n_3/n_4)v_3 + v_4} = \frac{1}{1 + (2k_3/k_4)\exp(\beta_3 VF/RT)} \quad (13)$$

The ratio of coulombic yields is

$$\frac{Q_C}{Q_D} = \frac{1 + (k_4/2k_3)\exp(-\beta_3 VF/RT)}{1 + (2k_3/k_4)\exp(\beta_3 VF/RT)} = (2k_3/k_4)\exp(\beta_3 VF/RT) \quad (14)$$

Since the coulombic yield can be determined in many cases to better than 5%, its variation with potential, according to equation (14) could be observed over 150 mV or more.*

(c) If steps III and IV both depend on potential, but to different extents (i.e. $z_3 \neq 0$; $z_4 \neq 0$ and $\beta_3 z_3 \neq \beta_4 z_4$) we have

$$Q_C = \frac{1}{1 + (n_4 k_4 / n_3 k_3) \exp(\beta_4 z_4 - \beta_3 z_3) VF/RT} \quad (15)$$

*The coulombic yields serve in this case as diagnostic quantities to determine the path of the reaction. A transition from step II followed by step III to II followed by IV is, in fact, a change in mechanism and both reaction products will only be produced in appreciable amounts in the range of potential in which a dual mechanism^{5,9} occurs.

and

$$Q_D = \frac{1}{1 + (n_3 k_3 / n_4 k_4) \exp [- (\beta_4 z_4 - \beta_3 z_3) VF / RT]} \quad (16)$$

and the ratio of coulombic yield will be

$$Q_C / Q_D = (n_3 k_3 / n_4 k_4) \exp [(\beta_3 z_3 - \beta_4 z_4) VF / RT] \quad (17)$$

Equations 15 to 17 are of particular interest in cases where the rates of the two parallel reactions depend on potential to a slightly different extent. In this case one would expect a slow variation of Q_C and Q_D with potential over an extended potential region.

Case 2

Here we consider a case in which the reverse reaction for one of the parallel steps is still negligible while that for the other is not (e.g., $v_{-3} = 0$; $v_{-4} \neq 0$). Step II is assumed rate-determining as before.

(a) Similar to case 1a we assume first that both steps III and IV are purely chemical ($z_3 = z_4 = 0$). Then

$$Q_C = \frac{v_3}{v_3 + v_4 - v_{-4}} = \frac{k_3}{k_3 + k_4 - k_{-4}} \frac{[D]}{[B]} \quad (18)$$

Substituting the steady state value of $[B]$ from equation (7) and rearranging we obtain

$$Q_C = \frac{k_3}{k_3 + k_4} \left[1 + \frac{k_{-4} [D]}{k_2 [A]} \exp(-\beta_2 VF / RT) \right] \quad (19)$$

also

$$Q_D = \frac{v_4 - v_{-4}}{v_3 + v_4 - v_{-4}} = \frac{k_4 - k_{-4} [D] / [B]}{k_3 + k_4 - k_{-4} [D] / [B]} \quad (20)$$

and upon substitution from equation (7) we find

$$Q_D = \frac{k_4}{k_3 + k_4} \left[1 - \frac{k_3 k_4 [D]}{k_2 k_4 [A]} \exp(-\beta_2 VF/RT) \right] \quad (21)$$

Thus the coulombic yields are dependent on potential though the rates of steps III and IV are not directly potential dependent.

(b) If Step III is electrochemical but step IV is chemical

(i.e. $z_3 = 1$, $z_4 = 0$; $n_3 = 2$, $n_4 = 1$) we have

$$Q_C = \frac{v_3}{v_3 + (v_4 - v_4)/2} = \frac{k_3 \exp(\beta_3 VF/RT)}{k_3 \exp(\beta_3 VF/RT) + (k_4/2) + k_4 [D]/2[B]} \quad (22)$$

Substituting again the steady state value of $[B]$ from equation (7) and rearranging we have

$$Q_C = \frac{k_3 \exp(\beta_3 VF/RT)}{k_3 \exp(\beta_3 VF/RT) + k_4/2} \left[1 + \frac{k_4 [D]}{2k_2 [A]} \exp(-\beta_2 VF/RT) \right] \quad (23)$$

and

$$Q_D = \left[\frac{k_4}{k_3 \exp(\beta_3 VF/RT) + k_4/2} \right] \times \left\{ 1 - \frac{k_3 k_4 [D]}{k_2 k_4 [A]} \exp[(\beta_3 - \beta_2)VF/RT] \right\} \quad (24)$$

COMPARISON WITH EXPERIMENT

During the study of the mechanism of the anodic oxidation of butadiene and benzene on platinized Pt electrodes¹⁰ the coulombic yield for CO_2 production was determined at a number of current densities. These results are shown in Fig. 1a and 2a. The corresponding partial current densities, defined as the product of coulombic yield and total current density at which it is measured is plotted in Fig. 1b and 2b as a function of potential. Fig. 3 shows, for comparison, the values of the partial current densities as a function of potential calculated

from equations (12) and (13). The similarity between Fig. 2b and Fig. 3 is rather striking if we recall that a simple three step reaction was assumed here for the purpose of calculation, while the oxidation of benzene involves thirty charge transfer steps and proceeds through a very complex reaction path.

CONCLUSIONS

The coulombic yield is potential dependent in most cases over a limited potential range (0.1 - 0.2 volts, depending on the accuracy with which it is determined) and unity outside this range. Care must be exercised in evaluating the exchange current density of a reaction when a coulombic yield of less than unity is observed. Thus the extrapolation of the observed current density to the reversible potential calculated for complete combustion of butadiene to CO_2 gives the correct exchange current density for this reaction, as can be seen from Fig. 1b. In the case of benzene, however, a similar procedure is entirely invalid (cf. Fig. 2b) since, as the reversible potential is approached, the fraction of the reaction forming CO_2 becomes exceedingly small.

In electro-organic synthesis the yield of a desired product may be increased by operating at a different potential, changing the temperature¹¹ or changing the concentrations of reactants in solution (cf. equation 19 or 23).

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CAPTIONS TO FIGURES

- Fig. 1a: The coulombic yield for CO_2 production and the ratio of coulombic yields on the anodic oxidation of butadiene on platinized Pt electrodes as a function of current density.
- Fig. 1b: Overall and partial current densities in the anodic oxidation of butadiene on platinized Pt electrodes as a function of potential.
- Fig. 2a: The coulombic yield for CO_2 production and the ratio of coulombic yields in the anodic oxidation of benzene on platinized Pt electrodes as a function of current density.
- Fig. 2b: Overall and partial current densities in the anodic oxidation of benzene on platinized Pt electrodes as a function of potential.
- Fig. 3: Calculated partial current densities equation 14 plotted as a function of potential.

FIG. 1a

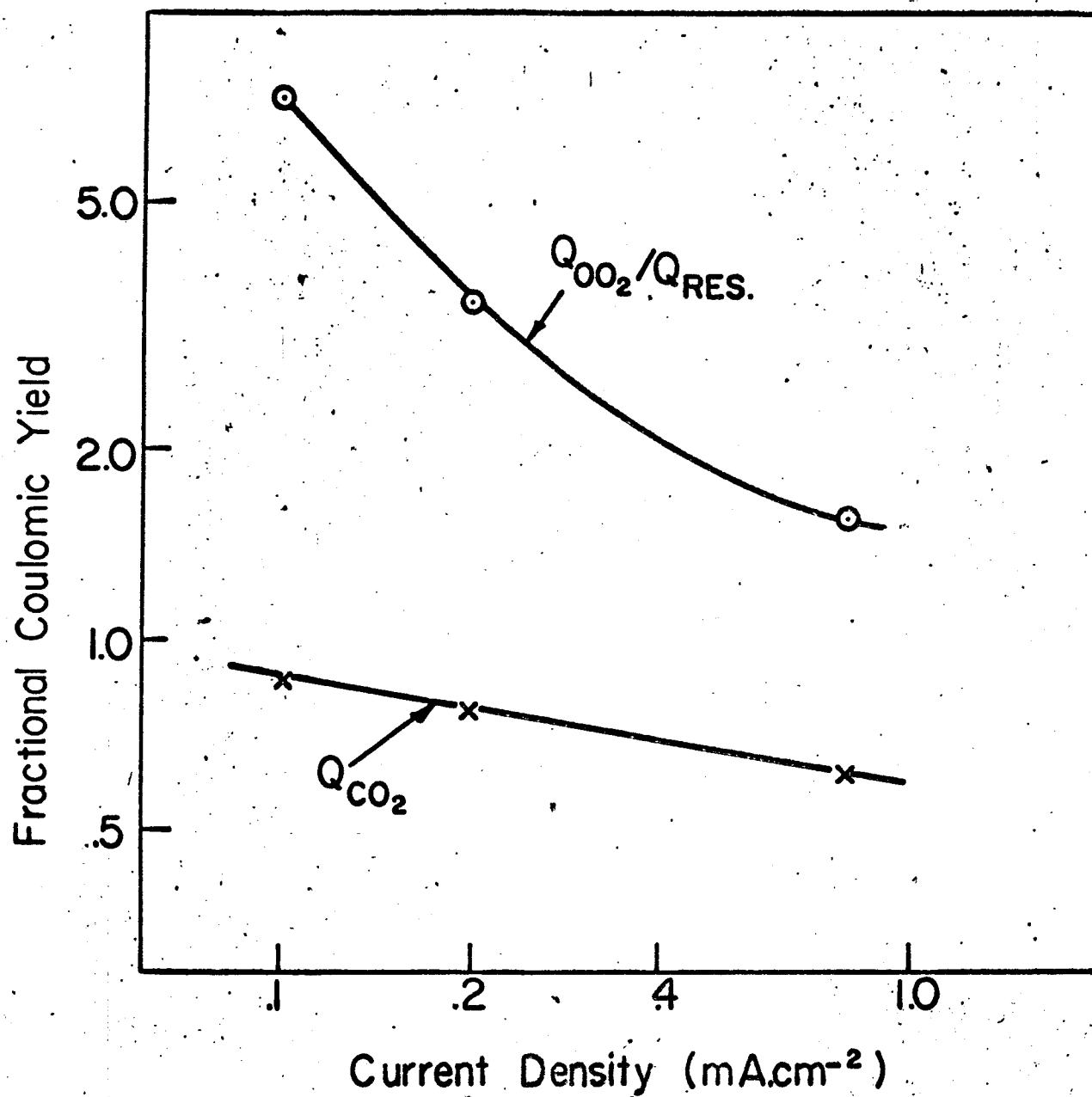


FIG. 2a

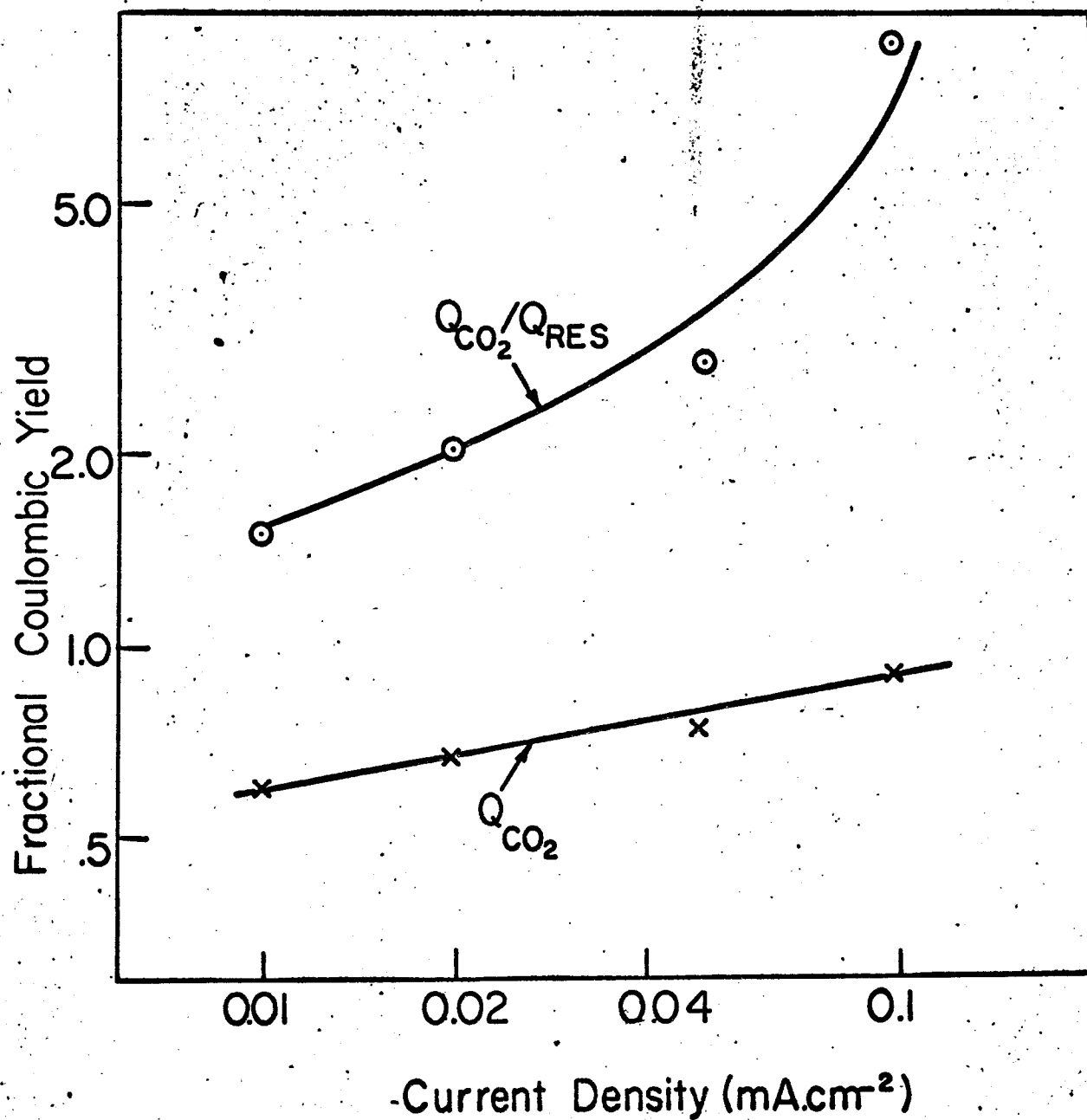


FIG. 1b

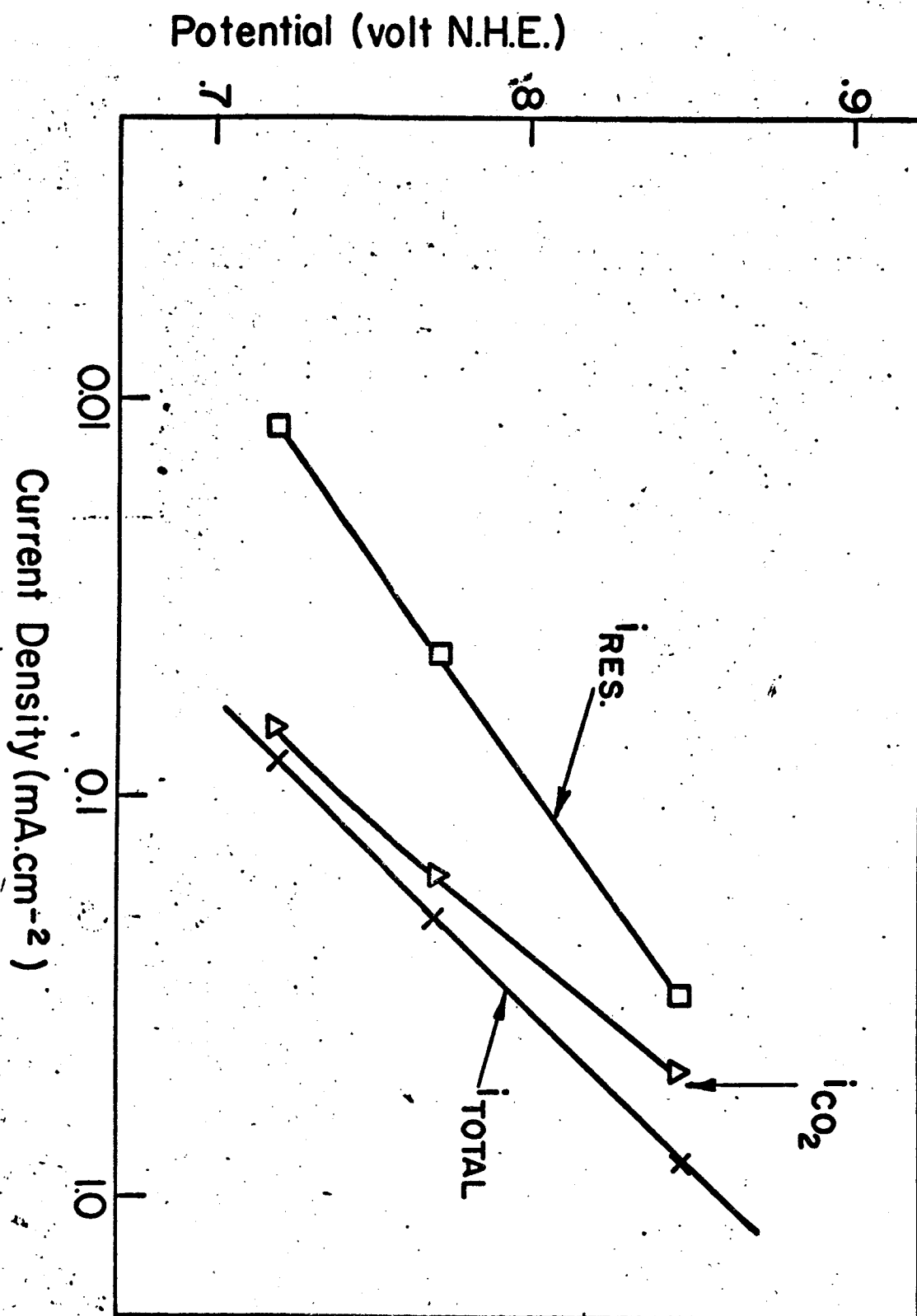
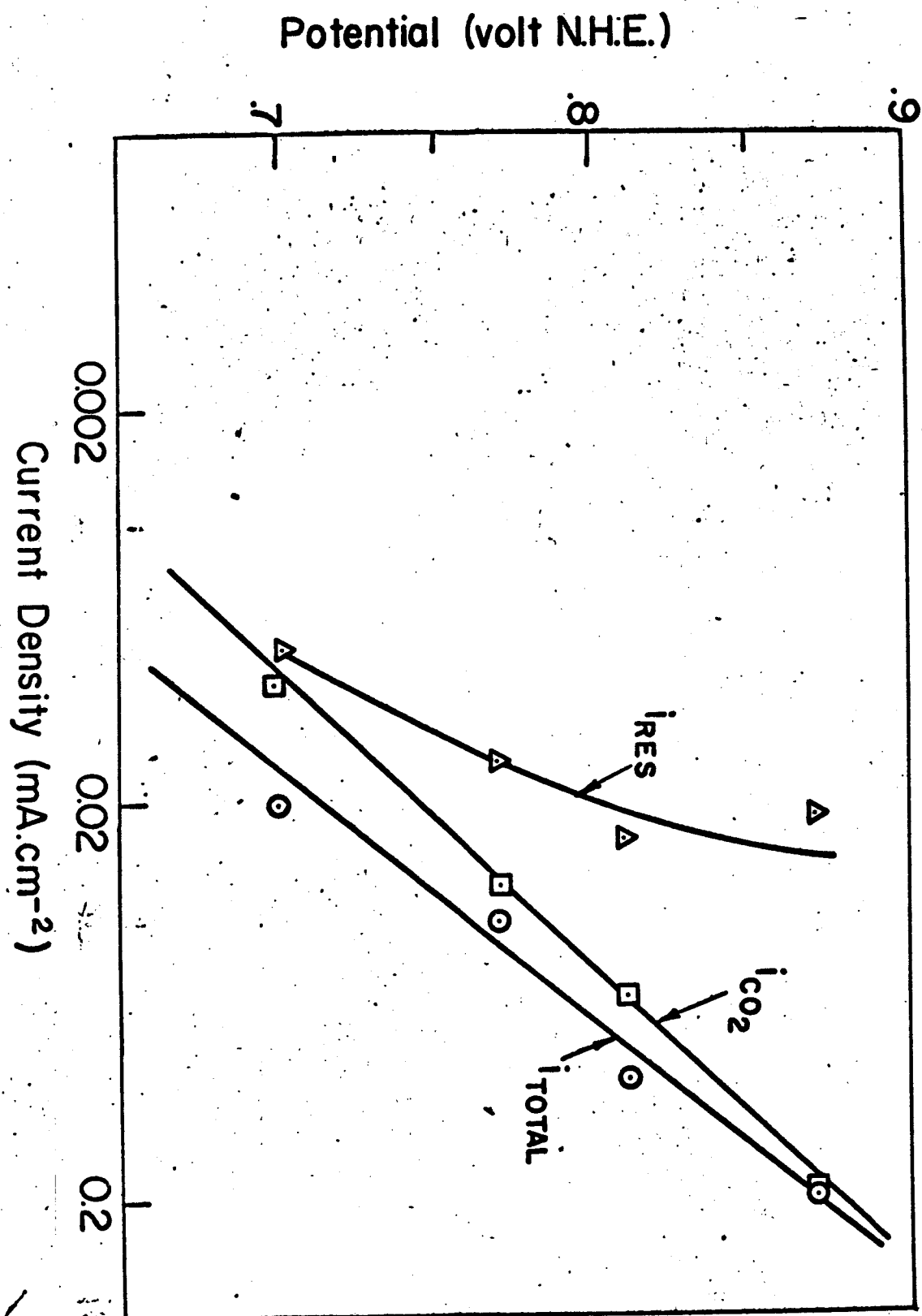
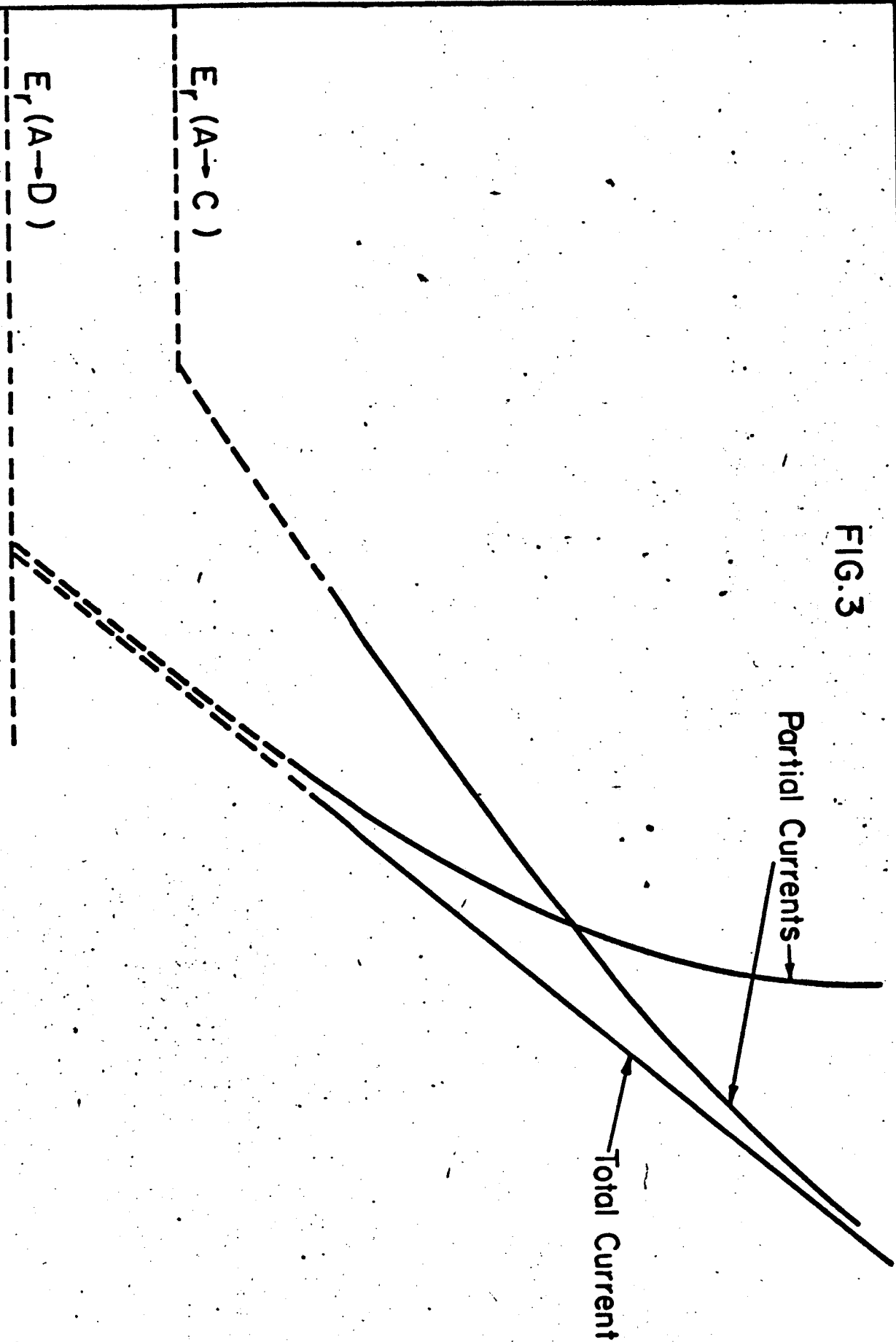


FIG.2b



Potential (Arbitrary Units)

FIG. 3



$\log i$ (Arbitrary Units)